WILEY

HANDBOOK OF VINYL FORMULATING

SECOND EDITION

EDITED BY
RICHARD F. GROSSMAN

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Richard F. Grossman, Series Editor

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WILEY SERIES ON PLASTICS ENGINEERING AND TECHNOLOGY

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PREFACE TO THE SECOND EDITION

As Ed Wickson stated in the Preface to the First Edition, the *Handbook of Vinyl Formulating* is the only text devoted to that topic. It has been highly successful; copies are in the hands of most of the vinyl technologists in North America and many throughout the world. Vinyl formulating has developed considerably in a number of areas since 1993. The Second Edition addresses these developments.

Certain of the chapters of the First Edition have been combined. “Antidegradants,” for example, covers antioxidants, heat stabilizers, light stabilizers and biocides. The reason is that, in formulating, the technologist must consider all of these in developing a stabilization package. Presentation in a single chapter enables correlation without repetition. Similarly, “Fillers and Reinforcements” combines several chapters. The technologist is encouraged not to look at individual ingredients but to look at all in a given class, to experiment with several and, when needed, to innovate useful blends. To this end, suggestions are included regarding experiments that have not as yet been reported but that seem interesting.

There has been a conscious effort to avoid material better suited to more specialized texts in order to concentrate on formulation. This does not include rationalization as to why ingredients have the effects observed, since such theorizing is vital to innovation. Another factor important in product development is intellectual satisfaction. To that end, authors and editor have done their best not to be boring.

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PREFACE TO THE FIRST EDITION

Although superseded by polyethylene as the world's number one plastic, polyvinyl chloride (PVC) retains its title as the most versatile of all plastics—both in the number of ways it can be processed and in the range of end products. This is due to (a) the wide variety of PVC resin types available (varying in molecular weight and distribution, homo-, co-, and terpolymers, particle size and distribution, morphology, crystallinity, etc.) and (b) the ability of PVC to be formulated with a multitude of additives, unmatched by any other plastic.

There is a wealth of information on PVC technology available in various scientific and trade journals, proceedings of technical meetings, and technical literature of suppliers of PVC resins and additives. There are also several excellent books on the broad aspects of PVC technology and on additives for plastics. However, none focuses on PVC formulating. This volume is the end result of what the editor had long felt was a need for a one-volume, ready-reference book describing in detail the properties of the various commercial PVC resins available in the United States and Canada and how these, together with additives, are used in formulating PVC. Related chapters cover economics of formulating, basic statistics and design of experiments, laboratory compounding and test methods, and environmental and health concerns in formulating vinyl compounds. Although emphasis is on formulating in this book, separate chapters are also included on dry blending, powder coatings, plastisol and organosol preparation, and electron beam radiation curing because these are not all covered in currently available books.

Because of its complexity, there is probably no one person who could claim to be truly expert on all aspects of the resins and additives used in PVC formulating. With this in mind, the editor chose experts well qualified in their particular field to author the various chapters. The reader is encouraged to contact these experts for additional information.

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Baton Rouge, LA
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CHAPTER 1

Formulation Development

EDWARD J. WICKSON and RICHARD F. GROSSMAN

1.1 INTRODUCTION

Polyvinyl chloride (PVC, vinyl) became a major factor in commercial manufacture of flexible goods after World War II, replacing rubber, leather, and cellulosics in many areas. As processing technology developed, unplasticized (rigid) PVC began expansion into replacement of metal, glass, and wood, a trend that continues and which now consumes the greatest part of PVC usage. The acceptance of PVC is based on its performance-to-cost ratio. A broad range of useful properties, such as stability, weatherability, inertness to many media, and inherent flame and microbial resistance, are available, with proper formulating, at low cost.

PVC is the thermoplastic polymer most easily varied in properties through formulation. Filler levels vary from a few parts per 100 of resin (phr) in pressure pipe to hundreds of phr in extruded cove base or calendered floor tile. The latter could reasonably be described, based on the most prevalent ingredient, as marble rather than vinyl flooring. In other applications, plasticizer levels as high as 70 phr are common. PVC compounds invariably contain heat stabilizers and lubricants (or ingredients that do both). They may contain fillers, plasticizers, pigments, antioxidants, biocides, flame retardants, antistatic agents, impact modifiers, processing aids, and other

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ingredients, including other polymers. Formulation is therefore complex. The goal of this text is to make the process easier to understand and carry out.

1.2 EFFECTS OF FORMULATION ON PROCESSING

The aim of the formulator should be to develop a robust compound, that is, one that will process satisfactorily and yield acceptable properties even if processing or service conditions deviate from those anticipated or thought ideal. This must be done within certain cost parameters. Therefore, the goal, in practice, is to develop the best compound that the application can afford. This should be considered rational formulating. The alternative—development of the lowest-cost compound that can possibly be processed or manage to conform to expectations in testing or service—usually creates more problems than it solves. Although this text is directed primarily to the formulator of rational compounds, it is anticipated that others, radically constrained by cost considerations, may find guidance as well.

The formulation that is optimum today may not be so next year. If it is optimum in one plant, even on one processing line, it may be less so on another. The adaptability of PVC to various processing techniques is stimulation to the ingenuity of the plastics engineer. PVC compounds are calendered, extruded, molded by various techniques, coated, and cast. In these applications, processing begins with a blending step in which additives are mixed with PVC resin. The result may be a (more or less) dry blend, plastisol, organosol, blended latex, or solution. The blending step is followed by fluxing and fusion in the product-forming step (usually the case with rigid PVC) or in a separate pellet-forming step prior to product manufacture. The latter is common with plasticized (flexible) PVC, particularly if the pelletized compound is to be transported to another location, for example, the factory of a customer.

The rate of dry blending can be of concern if it is output-limiting. Although this may be affected by a number of ingredients, it is primarily dependent on the PVC resin and particular plasticizer. Certain resins are designed for rapid plasticizer uptake. Plasticizer type (polarity), viscosity, and solvent power are key factors. These, however, are usually determined by the application rather than ease of incorporation. Typically, processing is adjusted to suit the formulation, by such steps as preheating the plasticizer and following a judicious order of addition of ingredients. Dry blending and blending of solution vinyl, latexes, plastisols, and organosols are discussed in specific chapters of this book.

The resin is of key importance, whether fluxing rigid or flexible compositions. Examples of fast-fluxing resins include low-molecular-weight (low *K*-value) homopolymers and vinyl acetate copolymers. Plasticizers that are strongly solvating, such as butyl benzyl phthalate (BBP), increase flux rate. Again, the selection of both resin and plasticizer is usually dictated by the application. Therefore, the choice of other ingredients, particularly lubricants, stabilizers, and processing aids, is used to increase or decrease the rate of fusion.

In large-volume rigid PVC applications, dry blend is used directly to manufacture articles such as pipe, siding, and window profiles. Certain high-volume flexible applications, such as extrusion of wire coverings, are also often run from dry blend. Most flexible compounds are, however, fluxed and pelletized, using the combination of an internal batch mixer and a pelletizing extruder, an extruder that can do both, or a combination of extruders. In melt processing, viscosity and friction with metal surfaces are not only obvious factors needed for fusion and pellet formation, but also limitations of output, causes of equipment wear, and potential sources of PVC degradation. This, of course, is also the case with processing to form specific articles. All of the above are influenced critically by formulation and by selection of processing equipment. The extremes of the interaction of formulation and processing in the thought processes of formulators are as follows:

1. The optimum compound having the best available properties-to-cost ratio is developed. Then processing equipment yielding the greatest output and consistency is put into place and duplicated as new facilities are built. This scenario is the case with most high-volume rigid PVC applications and underlies the rapid growth of this sector in North America. A consequence is that suppliers of equipment and of ingredients are driven to cooperate by development of new and improved products.
2. At the other extreme, formulation is continued, often endlessly, to generate compounds that manage to conform to product expectations after on-the-edge processing, using a variety of equipment that happens to be on hand, or that may be obtained at the lowest investment. This is the case with certain flexible PVC applications. It is an important cause of market share decline from offshore competition and displacement of PVC by newer systems, for example, by thermoplastic elastomers.

1.3 EFFECTS OF FORMULATION ON PROPERTIES

In unplasticized compounds, structural rigidity (flexural strength) increases with increasing molecular weight (MW). Up to a point, filler addition increases flexural strength, while impact modifiers and processing aids tend to cause a decrease unless they also function as heat distortion improvers.

Tensile strength, on the other hand, tends to level off as MW is increased, although low extension modulus parallels flexural strength. Abrasion and creep resistance, as with plastics generally, increase with increasing MW, as does cut through resistance. Filler addition can improve both properties to the extent to which particle size and shape create structure in the composition.

Chemical and oil resistance also improve with increasing MW, as does resistance to heat distortion. The attributes that decline with increasing MW are, of course, output and ease of processing. Thus, formulation includes the use of additives that improve the flow of compositions based on high-MW resin, and those that tend to compensate for the choice of a lower-MW alternative. It has, in fact, been suggested that a key purpose of additives is to correct problems introduced by other additives.[1]

Compounds containing about 25 phr active plasticizer, such as di-2-ethylhexyl phthalate (DOP:100 percent tensile modulus about 3300 psi) are considered semirigid. Low extension tensile modulus is a reasonable measure of the flexibility of plasticized PVC. It increases somewhat with increasing MW and decreases strongly with increasing plasticizer content. Above about 35 phr DOP, or plasticizer with comparable activity, PVC is considered flexible. At 50 phr, 100% tensile modulus has dropped to about 1700 psi, and at 85 phr, about 650 psi, indicating a highly flexible compound. Lower levels of a more efficient plasticizer will generate comparable data, while less efficient ones would have to be used at higher levels. In plasticized compounds, tensile strength increases more or less linearly with increasing resin MW. Plasticizer type and level have a more profound effect. Both tensile strength and elongation often, but not always, decrease with increasing filler level. Tear strength improves with increasing MW, as does abrasion resistance, but these also depend on the effects of additives. Copolymerization with vinyl acetate leads to similar effects as plasticizer addition, often with fewer associated side effects, but usually at higher cost.

The major factors affecting low-temperature brittleness and flexibility are the level and type of plasticizer. Compounds for low-temperature service most often use blends of standard with special-purpose low-temperature plasticizers (e.g., di-2-ethylhexyl adipate (DOA)). Plasticization typically decreases chemical, solvent, and oil resistance. This can be countered by use of polymeric plasticizers, with attendant increase in cost and typical loss of processing ease, or by means of blends and alloys with highly oil-resistant polymers such as acrylonitrile–butadiene rubber (NBR).

One of the major uses of flexible PVC is in wire coverings. The service rating determines the choice of plasticizer, chosen so as to resist volatilization during the heat aging tests needed to qualify. Loss of plasticizer is the major cause of decreased elongation after heat aging. For service in dry locations, most such compounds use calcium carbonate ($CaCO_3$) filler. The level is adjusted to balance material cost versus requirements such as abrasion and cut through resistance. Insulations for service in wet locations, where testing (in North America) requires stable volume resistivity for 6 months in 75 °C or 90 °C water, are best served instead with electrical grades of calcined clay. For such service, the plasticizer and other ingredients must be electrical grades. Long-term wet electrical requirements necessitate close quality control of all materials.

Plasticized PVC compounds can have flame resistance ranging from slow-burning, when flammable plasticizers are used, to self-extinguishing when compounded with the halogen synergist antimony oxide, flame-retardant plasticizers, and hydrous fillers such as aluminum trihydrate (ATH) or magnesium hydroxide. Although hydrous fillers add to heat stability, flame-retardant (FR) plasticizers usually require higher levels of stabilizer. Hydrous fillers also reduce smoke generation by promoting oxidation of hot carbon particles (water gas reaction). This reaction is thought to go through metal carbonyl intermediates and is catalyzed by compounds of metals that form carbonyls. The most commonly used is molybdenum, in the form of ammonium octamolybdate (AOM), which reacts at useful temperatures. Flame resistance is increased and smoke generation decreased by fillers that promote formation of a thermally conductive glassy char during combustion. These include hydrous fillers and certain zinc compounds, notably zinc borate and hydroxystannate. The use of zinc compounds typically requires higher stabilizer levels. This is not the case with antimony oxide, but its use increases smoke generation. Thus, the compounding of highly FR flexible PVC requires complex balancing of ingredients. The overall balance of physical and FR properties of suitably compounded FR flexible PVC is very much better than that of "halogen-free" polyolefin substitutes. The latter typically are so overextended with hydrous fillers that the polymer is no more than a binder.

Rigid PVC foamed composites, consisting of solid layers above and below a foam core, have become increasingly accepted in pipe, siding, and plastic lumber. In addition to weight and cost reduction, thermal conductivity of vinyl siding is decreased, and lumber products are more readily nailed or sawn. Flexible PVC foamed products are most often run from plastisols, as in continuous vinyl flooring, and may be made mechanically by introducing air with strong agitation, or chemically with blowing agents, most often azodicarbonamide. The latter is readily activated by a number of additives, often components of the heat stabilizer, known in such cases by the jargon "kicker." Surfactants are used to improve cell structure quality, which is also dependent on resin and plasticizer choice.

Light stability and weatherability are provided in a number of ways. The outer layer (topcoat) of vinyl siding or window profile will contain sufficient titanium dioxide (TiO_2) of a suitable grade. Its high dielectric constant enables absorption of a quantum of light and dissipation of energy as heat before a lower-energy photon is emitted. This limits the extent to which incident light is capable of initiating chain reaction free-radical oxidation. Carbon black, again of suitable grades, has the same effect and is widely used in cable jackets and agricultural sheeting. It is, of course, useful to have products that are other than white, black, or gray. Pigments that behave similarly to TiO_2 are used in vinyl siding provided in colors. Other strategies include use of light-resistant topcoats such as acrylics and polyvinyl difluoride (PVDF) over a PVC substrate. Acrylic coatings are also used over PVC plastisol impregnated polyester mesh in flexible signage backgrounds to provide improved printability and resistance to plasticizer migration as well as light stability. In such cases and in other clear and brightly colored products, organic ultraviolet (UV) light absorbers are included. These function in an analogous manner to carbon black and TiO_2. A photon of light is absorbed, driving the UV light absorber into an excited state. The latter is resonance-stabilized and persists long enough to dissipate energy as (more or less) harmless heat. Additives that are strictly light absorbers, such as hydroxybenzophenones and benzotriazoles, are not antioxidants—in fact, they require antioxidant protection. A newer class of materials, hindered amine light stabilizers (HALS), are not only antioxidants but participants in a chain-reaction antioxidant action. The use of HALS in PVC is now in exploratory stages.

Weatherability of PVC compounds is studied in a variety of devices that simulate sunlight. There is only relative correlation between these methods and actual outdoor exposure. The effects of outdoor exposure itself vary from location to location. There is even suspicion that accelerating outdoor aging using magnification of sunlight introduces variability. Nevertheless, these methods are useful in comparing one compound with another, and the results are often thought predictive of field service by product manufacturers. Field service in plasticized compounds is also prejudiced by microbial attack in humid locations. Since it is often impossible to predict service conditions, the use of biocides in flexible compounds is common.

The mixing of particulate and low-MW ingredients into polymeric compositions leads one to consider the conditions under which they might overcome the entropy gain of mixing, that is, unmix. This can occur in both dynamic and static situations. In turbulent flow, the lowest-energy state is often stratification rather than homogeneity. Deviation from streamline flow in processing equipment, if severe enough, can cause partial fractionation of compounds. This is a driving force leading to plateout on equipment surfaces and deposition of ingredients on extruder screens. The rate of separation from a mixture (the instability of a phase) is a function of the density of the ingredient. Thus, the ingredient found first on the screenpack is the lead stabilizer or its reaction product, or (in otherwise stabilized compositions) titanium or zinc. If barium is present in the stabilizer, it is typically the ingredient that must be protected from plateout. Turbulent flow cannot be completely avoided. It is, in fact, a desirable feature of mixing because of its action in breaking up agglomerates (filler dispersion). It should, however, be minimized during product formation. This will aid in formulating towards the best possible cost-to-properties ratio.

A second area of concern is whether ingredients will stay put during service. Surface oxidation of siding or profile, for example, may cause a case-hardening effect through crosslinking. The result of the resultant increased surface modulus is to make inclusions less compatible, leading to “chalking,” generally of the most dense species, TiO_2. This may or may not be thought desirable. In flexible PVC, plasticizer remains homogeneously distributed (except under severe turbulent flow) because of dipole–dipole attraction to the polymer. But will this be the case if an object having high plasticizer solubility, such as polystyrene or a pressure-sensitive adhesive, is in contact with the plasticized PVC article? Migration can be minimized by formulation with polymeric plasticizers, as in refrigerator gaskets and pressure-sensitive tapes, or by use of NBR or ethylene vinyl acetate (EVA) alloys to achieve flexibility. The plasticizer may carry other ingredients to the surface, which can contribute to taste and odor from food packaging film, bottle cap liners, or refrigerator parts. Occasionally, this feature is put to good use, as in self-cleaning flooring topcoats, where the plasticizer is chosen to have slight outward migratory tendency, limiting the penetration and facilitating the removal of oily dirt.

Plasticizer migration is also a concern in medical and food packaging applications. Despite the migratory potential of DOP in medical devices and of DOA and DOP in food packaging applications, the history of safe usage, low cost, and expense of obtaining regulatory approval have worked against the adoption of technically more suitable plasticizers. These are some of the most common questions encountered with the invention of a new or improved ingredient:

- Will its use be cost-effective?
- Can long-range service performance be assured?
- Can approvals be secured?

The last of these is a reminder that effective formulation cannot be carried out in a vacuum. There must be input from and cooperation by all departments of the prospective supplier of a new additive.

The above generalizations are admittedly oversimplified and will be amplified in the chapters to follow.

1.4 COMPOUND DEVELOPMENT PROCEDURE

If the application in mind is new or a new use, it is necessary to make sure that dated records of formulation development and testing are kept, in light of potential patentability. If there are similar products in the field, their advantages and limitations must be considered. One should list the characteristics that would be ideal (sometimes they may be within reach) and discuss with marketing what considerations would lead to acceptance of the product. One should, further, consider the relation between the project in mind and others that have been worked on, and work by others of which one is aware. Consideration before plunging in can be very valuable. It is often possible to make an educated guess as to the most promising solution before beginning experimentation. These steps are part of design of experiments, even though difficult to formalize.

This should be followed by a review of specifications for the product. These include not only documents from regulatory agencies, but also statements of customer requirements or samples of competitive articles. One should be sure that test methods are specified in adequate detail. In some instances, starting-point formulations can be taken from suppliers' literature (or sources such as this text). Ingredient suppliers are often willing to cooperate in a program of testing. On the other hand, there are applications in which the formulator desires to have as little outside awareness of the program as possible. This must be balanced against the fact that with modern analytical equipment and sufficient effort, all compositions can be reconstructed.

At this point, a program of experimentation can be designed, either informally (which is usually the case when the general area is well known) or statistically (which is common when one is at the edge of known technology). In the most common instance, the actual experimental work is likely to be carried out by a technician (while the investigator is involved in nontechnical tasks). The instructions to the technician should indicate the most likely outcome of the experiments, so that unexpected results can be appreciated and reported promptly. It is with the unexpected that we learn. The successful innovator follows Pasteur's dictum that chance favors the well prepared. To make such observations, it is, of course, better to run the experiments oneself (except in cases where one anticipates that the technician will do more careful work).

One should record mixing conditions where possible, noting time–temperature characteristics of the blending and fluxing stages. These can be checked versus running the same composition in a torque rheometer. Full fusion is necessary if original and heat-aged physical properties are to be meaningful. When obtaining tensile data, particularly in comparison with control or competitive samples, it is best to run the entire stress–strain curve rather than noting merely data at break or yield points. The experienced chemist can deduce differences in formulation from characteristics of the shape of such curves. If a sample shows a major excursion from average data, it is useful to try to determine the reason. For example, an unusually poor value for tensile strength combined with more or less normal 100 percent modulus is a clue to search the sample break for undispersed ingredients. (An unusually high value of tensile strength would of course be more provocative.)

Finally, one should examine the results of every program of experimentation to determine whether they would instead, or in addition, apply well to some other problem of interest—perhaps one that refused facile solution in the recent past.

1.5 COST OF INGREDIENTS

Although a few ingredients (e.g., hydrocarbon oils) are sold by volume, most are purchased by weight, as is custom-mixed compound. On the other hand, vinyl articles are sold on a volume basis. Thus, materials cost must also be known per standard volume. Throughout most of the world, this is the liter. The formula weights (kg) of ingredients are divided by their densities to yield volumes of each. The total volume and total weight ratio yields the calculated (or theoretical) density of the composition. In the United States, it is common to express recipe weights in lbs. The associated volume is the lb/volume. It is most often calculated by divided the formula weight by the specific gravity, the ratio of its density to that of pure water at a given temperature. Specific gravity (SpG) is therefore dimensionless, and lb/volume (or kg/volume) merely a construct. Since the difference between density and SpG is typically small, the calculations remain meaningful.

In unplasticized PVC, calculated SpG should compare quite closely to that measured on the finished article. Deviations on the low side suggest porosity or incomplete fusion and, therefore, make the observation well worthwhile. If, on the other hand, a foamed structure is intended, the measurement is even more significant. Plasticized PVC articles should have a SpG slightly higher than that calculated, depending on the level of plasticizer. This is a solvation effect that is well known.[2] If there is no such effect, that is, there is a substantial plasticizer level but complete agreement (to 0.001) between observed and calculated SpG, one should (after repeating the calculation) check thoroughly for plasticizer migration tendency. In general, one should check SpG routinely as an estimate of correct formulation before spending time with physical testing. A corollary is to check mass balance periodically, that is, to check that the decrease in inventory of resin and other ingredients corresponds to the quantity of compound produced.

Plasticizer loss can occur through volatilization during processing, particularly during fusion of plastisol coatings. Here losses can be in the range of several percent. This may be unavoidable because of product requirements, but must be considered in cost calculations, and in design of pollution controls. To assist in cost calculations, the specific gravities of common ingredients have been listed in the following section.

TABLE 1.1 Specific Gravity of Polymeric Ingredients

PVC homopolymer	1.40
PVC/vinyl acetate (VA), 2% VA	1.39
PVC/VA, 5% VA	1.38
PVC/VA, 10% VA	1.37
PVC/VA, 15% VA	1.35
Acrylic impact modifier	1.10
Acrylic processing aid	1.18
Acrylonitrile butadiene styrene (ABS) impact modifier	0.95–1.04
Methacrylate butadiene styrene (MBS) impact modifier	1.0
Poly(α-methylstyrene)	1.07
Chlorinated polyethylene (CPE), 42% Cl	1.23
Chlorosulfonated polyethylene (CSM)	1.18
NBR, medium acrylonitrile (ACN)	0.99
PVC/polyurethane (PU) blends	1.3–1.4

1.6 SPECIFIC GRAVITY OF INGREDIENTS

SpG of polymeric ingredients is given in Table 1.1. SpG of phthalate plasticizers is given in Table 1.2, that of speciality plasticizers in Table 1.3, and that of miscellaneous plasticizers in Table 1.4. SpG of commonly used organic additives is given in Table 1.5 and that of inorganic additives in Table 1.6.

TABLE 1.2 Specific Gravity of Phthalate Plasticizers

Dibutyl (DBP)	1.049
Diisobutyl (DIBP)	1.042
Butyl octyl (BOP)	~1.0
Dihexyl (DHP)	1.007
Butyl benzyl (BBP)	1.121
Dicyclohexyl (DCHP)	1.23
Di-2-ethylhexyl (DOP)	0.986
Diisooctyl (DIOP)	0.985
Dicapryl (DCP)	0.973
Diisononyl (DINP)	0.972
Di-trimethylhexyl	0.971
C_9 linear	0.969
Diisodecyl (DIDP)	0.968
C_7–C_9 linear	0.973
n-C_6–C_{10} (610P)	0.976
n-C_8–C_{10} (810P)	0.971
C_{11} linear (DUP)	0.954
Undecyl dodecyl (UDP)	0.959
Ditridecyl (DTDP)	0.953

TABLE 1.3 Specific Gravity of Specialty Plasticizers

Di-2-ethylhexyl adipate (DOA)	0.927
Diisooctyl adipate (DIOA)	0.928
Diisodecyl adipate (DIDA)	0.918
n-C_6–C_{10} adipate (610A)	0.922
n-C_8–C_{10} adipate (810A)	0.919
Di-n-hexyl azelate (DNHZ)	0.927
Di-2-ethylhexyl azelate (DOZ)	0.918
Diisooctyl azelate (DIOZ)	0.917
Dibutyl sebacate (DBS)	0.936
Di-2-ethylhexyl sebacate (DOS)	0.915
Diisooctyl sebacate (DIOS)	0.915
Tri-2-ethylhexyl trimellitate (TOTM)	0.991
Triisooctyl trimellitate (TIOTM)	0.991
n-C_8–C_{10} trimellitate (NODTM)	0.978
Triisononyl trimellitate (TINTM)	0.977
2-Ethylhexyl epoxytallate	0.922
Epoxidized soybean oil	0.996
Epoxidized linseed oil	1.034

TABLE 1.4 Specific Gravity of Miscellaneous Plasticizers

Tricresyl phosphate (TCP)	1.168
Tri-2-ethylhexyl phosphate	0.936
Ethylhexyl diphenyl phosphate	1.093
Isodecyl diphenyl phosphate	1.072
Isopropyl diphenyl phosphate	1.16–1.18
Acetyl tributyl citrate	1.05
Chlorinated paraffin, 42% Cl	1.16
Di-2-ethylhexyl isophthalate (DOIP)	0.984
Di-2-ethylhexyl terephthalate (DOTP)	0.984
Dipropylene glycol dibenzoate	1.133
Isodecyl benzoate	0.95
Propylene glycol dibenzoate	1.15
Hercoflex® 707	1.02
Nuoplaz® 1046	1.02
Trimethyl pentanediol diisobutyrate (TXIB)	0.945
Polyester, low MW	1.01–1.09
Polyester, medium MW	1.04–1.11
Polyester, high MW	1.06–1.15
Naphthenic oil	0.86–0.89
Alkyl phenyl sulfonate	1.06

TABLE 1.5 Specific Gravity of Organic Additives

Ethylene bis(stearamide) (EBS)	0.97
Calcium stearate	1.03
Glycerol monostrearate (GMS)	0.97
Paraffin wax	0.92
Low-MW polyethylene (PE) wax	0.92
Oxidized PE wax (OPE)	0.96
Mineral oil	0.87
Stearic acid	0.88
Bisphenol A	1.20
Topanol® CA	1.01
Irganox® 1010	1.15
Irganox® 1076	1.02
Benzophenione UV light absorbers	1.1–1.4
Benzotriazole UV light absorbers	1.2–1.4
Hindered amine light stabilizers (HALS)	1.0–1.2

TABLE 1.6 Specific Gravity of Inorganic Additives

Calcium carbonate	2.71
Talc	2.79
Calcined clay	2.68
Barytes	4.47
Mica	2.75
Alumina trihydrate (ATH)	2.42
Antimony trioxide	5.5
Antimony pentoxide	3.8
Magnesium hydroxide	2.4
Basic magnesium carbonate	2.5
Molybdenum oxide	4.7
Zinc borate	2.6
Carbon black	1.8
Titanium dioxide	3.7–4.2

1.7 DESIGN OF EXPERIMENTS

Experimentation has two general goals: an improved understanding of how and why effects occur, generally thought of as mechanism; and development or improvement of specific products and processes. Despite human attempts, the goals are inseparable. Understanding of the underlying physics and chemistry aids in problem-solving as surely as experimental results create and modify theoretical explanations. The vinyl formulator is urged to continue to read in the basic sciences and further, to proceed now to Chapter 22 for an expert's discussion of how to mechanize problem-solving.

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CHAPTER 2

Resin Selection for PVC Applications

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Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

2.1 INTRODUCTION

2.1.1 An Extremely Brief History of PVC

Vinyl chloride monomer (VCM) is believed to have been synthesized for the first time by Regnault in 1838. Regnault may have also been the first person to polymerize VCM when he noted that test tubes containing VCM formed a white powder when exposed to sunlight. The earliest recorded polymerization of VCM yielding polyvinyl chloride (PVC) was by Baumann in 1872.[1] The first scientists who attempted to examine the thermoplastic characteristics of PVC quickly discovered its annoying tendency to evolve hydrogen chloride when heated. Because of this, PVC was little more than a laboratory curiosity up through the early part of the 20th century.

The discovery of plasticizing agents for PVC by Waldo Semon of the BF Goodrich Company in the late 1920s and early 1930s permitted BF Goodrich to introduce PVC-coated fabrics into U.S. markets in 1931. The PVC/plasticizer blends were used to make products such as raincoats and umbrellas with a solvent-based casting process. About the same time, IG Farben was reported to have begun manufacturing similar products in Germany.[2] The subsequent development of suitable heat-stabilizing additives was the final technological development that enabled PVC to expand into other applications and become a commercially viable plastic. Flexible PVC became very important as a rubber substitute during the rubber shortages encountered during World War II. After World War II, the unique properties of flexible PVC enabled it to quickly find a plethora of other uses.

Dramatic advances in rigid PVC processing technology were made during the late 1940s and throughout the 1950s. This, coupled with similar advances in stabilizer, lubricant, process aid, and impact modifier additive technology, helped to facilitate the processing of rigid PVC compounds. Soon thereafter, rigid PVC gained a firm and rapidly growing foothold in markets previously dominated by materials such as wood, steel, and iron. At this time, major differences emerged between U.S. and European rigid PVC compound and process technologies. In the years following World War II, Europeans faced raw material shortages as their devastated chemical industry was being rebuilt. This led to an emphasis on tackling rigid PVC manufacturing issues through process and equipment technology. Since the U.S. chemical industry escaped the war relatively unscathed, U.S. development efforts tended to emphasize additive and formulation technology.[3] To this day, significant differences still exist between U.S. and European rigid PVC processing and formulation practice.

The other major chapter in the history of PVC involves the linking of VCM exposure to a rare form of liver cancer called angiosarcoma. In 1974, BF Goodrich announced that four of its workers had contracted angiosarcoma. All those afflicted were directly involved with the PVC resin manufacturing process. Shortly thereafter, abnormally high numbers of angiosarcoma cases were confirmed among employees of other PVC resin manufacturers throughout the world. Workers involved in the charging and cleaning of PVC reactors were especially prone to this type of cancer. VCM was identified as the culprit and PVC manufacturers rapidly implemented new manufacturing processes to greatly reduce worker exposure to VCM. PVC resin manufacturers also added a VCM stripping step in the manufacturing process, which virtually eliminated residual VCM in the PVC resin. The total number of angiosarcoma deaths attributed to VCM exposure worldwide is believed to number less than 150.[4] Since these manufacturing changes were implemented, no angiosarcoma cases have been linked to the manufacture of PVC resin. It is also important to note that no angiosarcoma cases have ever been conclusively linked to workers manufacturing products containing PVC resin.[5]

Total PVC resin production in the United States during 2003 was approximately 14.7 billion pounds.[6] About 14 billion pounds of this PVC resin production was homopolymer resin manufactured by either the suspension or mass polymerization process, with the suspension process accounting for the vast majority of this volume. An estimated 650 million pounds of dispersion, blending, copolymer, and other specialty PVC resins were also produced by the United States in 2003.[7] Total U.S. PVC resin production in 2004 increased 8.8 percent versus 2003 production to 16 billion pounds.[6]

2.1.2 Why is PVC Unique?

In the world of thermoplastics, PVC is a unique polymer. Unlike many of the commodity thermoplastics competing against it, PVC is primarily an amorphous material. However, most of the commercially available PVC resins contain crystalline regions ranging from 5 to 10 percent of the polymer. Although many of these crystalline regions melt at normal PVC processing temperatures, some remain intact at temperatures well over 200 °C.[8] The fact that some of these regions exist in plasticized PVC give polymer characteristics reminiscent to those of thermoplastic elastomers. These regions of crystallinity, along with the relatively narrow molecular weight distribution of PVC, help impart superior melt strength during extrusion and calendering processes versus other polymers.[9] The mostly amorphous nature of PVC also permits the cost-effective fabrication of clear articles in thicknesses exceeding 0.250 in (10 mm) with proper additive selection.

Another characteristic of PVC that makes it unique is that it contains approximately 57 percent chlorine by weight. This creates strongly polar regions within the polymer, which permits compatibility with a wide range of additives. No other commercially available polymer can have its properties modified in so many ways through the use of additives as PVC. The other unique characteristic imparted to PVC by chlorine is flame resistance. There are two primary mechanisms responsible for the inherent resistance of PVC to flame. When the PVC polymer decomposes due to heat released during combustion, hydrogen chloride forms and aids in the formation of char in the PVC polymer. Also, chloride-based radicals can find their way into the flame front during combustion and act as free-radical scavengers, thus reducing the efficiency of the combustion reactions.[10]

2.1.3 Structure of PVC

PVC is typically described by the following chemical structure:

$$\text{—(CH}_2\text{—CHCl)}_n\text{—}$$

PVC usually polymerizes in a "head-to-tail" arrangement; however, a small amount of branching is present in all commercially available PVC resin. The polymerized sequences tend to be atactic, but some syndiotacic sequences can form. These syndiotactic sequences are believed to be responsible for the regions of crystallinity found in PVC polymers. The amount of crystallinity present in the PVC polymer generally increases with molecular weight.[11] The molecular weight of the polymer can be controlled by both reaction conditions and reaction time. The ability to control the molecular weight of the polymer enables the manufacture of resins with a wide variety of properties. The polymerization process can also be modified to control crystallinity, resin particle size, plasticizer absorption, clarity, resin density, electrical conductivity, and a host of other properties.[12] The four main types of commercially available PVC homopolymer resins are suspension, mass, blending, and dispersion resins.

2.2 MANUFACTURE OF PVC RESIN

2.2.1 Suspension Resin Polymerization

After VCM is polymerized in a water suspension and the residual VCM is stripped, the resin is centrifuged to remove most of the remaining water, polymerization catalysts, and surfactants. The resin is then dried further, usually leaving a small amount of residual water on the resin particle surface to help dissipate static charges that can build up on the resin particle surface during handling. Other additives such as calcium stearate are sometimes added to the resin as well in order to improve its resistance to static charge buildup. The resin drying process must be carefully controlled so that the resin is not overdried and so that the unstabilized PVC resin particles do not undergo measurable degradation or discoloration due to excessive heat history in the drying process. The dried resin is then stored until it is shipped in bulk railcars or packaged per customer requirements. Most blending resins are also made by this process, the main differences being the smaller average size of the resin particle and the lack of resin particle porosity.[12]

2.2.2 Mass Resin Polymerization

Also referred to as "bulk" resins, mass resins differ from suspension resins in that they are not "suspended" in water during the polymerization process. Mass polymerization begins when initiators are added to VCM in the reactor. At the beginning of the process, VCM serves as the continuous phase. As polymerization progresses, phase inversion occurs and the PVC polymer itself becomes the continuous phase. Mass-polymerized resins are most commonly used in pipe applications, but sometimes find their way into other suspension resin applications.[12] Also, mass resins have the potential of offering improvements over suspension resins in terms of clarity and electrical properties due to the lack of suspending agents or other resin contaminants. However, mass resins are more likely to have gel contamination issues than suspension resins and tend to have worse initial color.[13]

2.2.3 Dispersion Resin Polymerization

There are significant differences between the suspension resin polymerization process and the dispersion resin polymerization process. The most apparent difference between the two resin types is the final particle size. The particle size of suspension resins range from 60 to 300 μm while the mean particle size of dispersion resins range from 0.2 to 1.5 μm.[14] Another major difference is that when the dispersion resin polymerization process is complete, the surfactant is usually not completely removed from the resin particle prior to drying. This residual surfactant greatly aids the dispersion of the resin in plastisol formulations and imparts a dramatic effect on plastisol rheology. These effects will be discussed in greater detail in Sections 2.8 and 2.9. The last major difference between suspension and dispersion resins is the low level of resin porosity, an important factor in the stability of viscosity and rheological properties of a plastisol in the unfused state over time.

2.3 EFFECTS OF RESIN SELECTION ON FLEXIBLE PVC COMPOUND PHYSICAL PROPERTIES AND MANUFACTURING PROCESSES

2.3.1 Physical Properties

2.3.1.1 Tensile Properties The tensile strength of flexible PVC is governed primarily by the amount of plasticizer in the formulation. However, the molecular weight of the resin also plays a role. As the molecular weight of the resin increases, there is a corresponding increase in tensile strength. This increase, when plotted versus intrinsic viscosity (IV), tends to be linear throughout the molecular weight range normally used in flexible PVC. The relationship between resin molecular weight and tensile strength is illustrated in Fig. 2.1. The tensile modulus behaves in a similar manner versus resin molecular weight.

2.3.1.2 Low-Temperature Properties Plasticizer selection and plasticizer level play a greater role in low-temperature property performance than resin selection for flexible PVC applications. However, intelligent resin selection can help to improve the low-temperature performance of flexible PVC compounds. Like tensile properties, the low-temperature performance of flexible PVC formulations can be improved by using higher-molecular-weight resins. Figure 2.2 demonstrates this relationship.

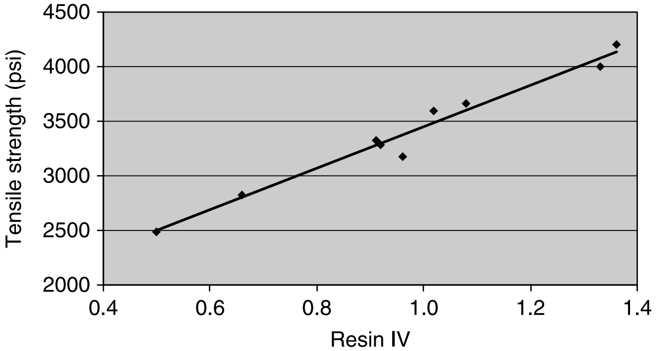

Figure 2.1 Effect of molecular weight on tensile strength of flexible PVC formulation. Formula in phr: PVC (various IVs) 100; DOZ 25; Tribase XL (Halstab) 7; $CaCO_3$ 5; Sb_2O_3 2; Plastiflow POP (Halstab) 0.2.

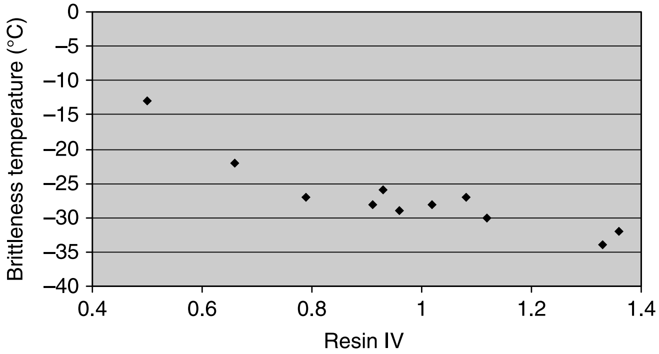

Figure 2.2 Effect of molecular weight on brittleness temperature of flexible PVC formulation. Formula in phr: PVC (various IVs) 100; DOZ 25; Tribase XL (Halstab) 7; $CaCO_3$ 5; Sb_2O_3 2; Plastiflow POP (Halstab) 0.2.

2.3.1.3 High-Temperature Performance Resistance to deformation at elevated temperatures is improved with higher-molecular-weight resins. Assuming that proper stabilizers and plasticizers are selected, higher-molecular-weight resins tend to outperform lower-molecular-weight resins under severe aging conditions at elevated temperatures. The exact reasons for this improvement are not known with certainty—some believe that higher-molecular-weight resins have a higher resistance to thermal degradation under static conditions. In order for this improvement in elevated-temperature aging performance to be seen, one must ensure that the higher-molecular-weight resin has not undergone excessive shear-related degradation during the manufacturing process.

2.3.1.4 Miscellaneous Properties As a rule, the resistance to chemical attack of PVC resin increases slightly as the molecular weight increases. Of course, plasticizer selection plays a far greater role in the chemical resistance of flexible PVC formulations than resin molecular weight. Outdoor weathering may see a slight performance boost with higher-molecular-weight resins. The belief behind this is that the deterioration of PVC physical properties during outdoor exposure is related to polymer chain scission phenomena. If the polymer starts the aging process with a higher average molecular weight, it will take longer for chain scission to reduce the average polymer molecular weight to the level where physical properties begin to diminish significantly.[15]

Resistance to abrasion, tear, creep, deformation at elevated temperatures, and flex fatigue resistance all improve with increasing resin molecular weight. Plasticizer compatibility also increases as molecular weight increases. Surface gloss tends to decrease with increasing molecular weight, but this property is also significantly influenced by processing conditions.

There is a key element that one must keep in mind. The improved physical property performance of higher-molecular-weight versus lower-molecular-weight resins is only valid if the higher-molecular-weight resin is properly fused and not significantly degraded during the manufacturing process. Poorly fused or significantly degraded PVC resins of any molecular weight will not perform well in most applications.

2.3.2 Manufacturing Processes

2.3.2.1 Plasticizer Absorption There are three main resin characteristics that control plasticizer absorption. The primary characteristic is the porosity of the resin particle, which controls the total amount of plasticizer absorbed (Table 2.1). Another characteristic is the actual size of the pores on the resin particle surface, which control the rate of absorption. The last factor is resin molecular weight, with higher-molecular-weight resin particles normally outperforming lower-molecular-weight particles in this regard. Porosity characteristics are controlled primarily by the PVC polymerization process. As a rule, the production of higher-porosity resins is less cost effective than the production of low-porosity resins.

2.3.2.2 Fusion Properties Fusion properties are governed primarily by plasticizer type and level as well as resin molecular weight. As the molecular weight of the resin increases, the fusion time increases. This is critical since the improved physical properties observed with higher-molecular-weight resins occur only when the higher-molecular-weight resins are sufficiently fused.

2.3.2.3 Melt Viscosity In addition to the contributions from the plasticizer, resin molecular weight has a significant effect on melt viscosity. As the molecular weight increases, the melt viscosity increases. This has a major impact on most manufacturing processes. The increased melt viscosity in most instances has a negative effect on output rates and sometimes requires that compounds based on higher-molecular-weight resins be processed at higher temperatures. The higher processing temperatures along with the increased shear encountered during processing often necessitate higher stabilizer levels along with changes in compound lubrication packages.

2.3.2.4 Melt Strength Increasing the resin molecular weight will also increase melt strength. This is important in many extrusion applications where extruded parts must not deform prior to cooling. Melt strength is also important in calendered

TABLE 2.1 Effect of Resin Porosity on the Powder Mix Time of PVC Resins

Plasticizer System	Geon 471, 1.02 IV, Porosity 0.50 cm^3/g	GP PVC Resin, 1.02 IV, Porosity 0.33 cm^3/g
DOP/ESO (45/20 phr)	229 s	320 s
TOTM/ESO (45/20 phr)	376 s	580 s
DOP/ESO (70/20 phr)	306 s	420 s
TOTM/ESO (70/20 phr)	520 s	No dry point

Source: A. C. Shah and D. J. Poledna, Review of Specialty PVC Resins, PolyOne Corp.

PVC applications where the film or sheet must maintain integrity in downstream manufacturing processes. It is also important in applications where the PVC is "drawn down" to the final dimensions as well as both thermoforming and blow molding applications.

2.3.2.5 Die Swell As resin molecular weight increases, die swell will decrease. Die swell is generally not a desirable characteristic, since it makes the fabrication of profile dies more difficult. The lower the die swell of a particular compound, the more easily a die can be fabricated on the first (or second) try. Compounds with lower die swell can also be extruded into complex profiles more easily than those with higher die swell.

2.4 EFFECTS OF RESIN SELECTION ON RIGID PVC COMPOUND PHYSICAL PROPERTIES AND MANUFACTURING PROCESSES

2.4.1 Physical Properties

2.4.1.1 Tensile Properties The effect of increased resin molecular weight generally has little effect on tensile strength and tensile modulus in rigid PVC formulations.[16] However, the tensile properties of rigid PVC formulations drop dramatically as the resin *K*-value decreases below 0.55. This reduction is due to the shorter PVC polymer chains present in very low-molecular-weight resins. It is believed that PVC tensile properties require chain entanglement in order for crystallite regions to form.[17] If the polymer chains are not long enough, crystallite regions have difficulty forming and significant tensile properties will not develop.

2.4.1.2 Impact Properties The impact properties of rigid PVC improve as resin molecular weight increases. There is also a similar improvement in low-temperature impact properties.[18] In order to achieve the impact property improvements afforded by higher-molecular-weight products, the resin must be properly fused. One must remember that many impact resistance failures in rigid PVC are not caused by formulation errors or poor resin selection choices, but by process-related issues.

2.4.1.3 Heat Distortion Properties Heat distortion properties of rigid PVC formulations tend to increase slightly as resin molecular weight increases. Normally additives like lubricants and stabilizers are of greater importance in determining the heat distortion temperature (HDT) of a rigid PVC compound. The loss of heat distortion properties begins to decrease at a faster rate when the resin *K*-value drops below 0.55 due to the chain entanglement phenomena (or lack thereof) described previously.

2.4.1.4 Miscellaneous Properties Rigid PVC compounds tend to have good solvent resistance properties versus many competing polymers. The resistance to chemical attack of rigid PVC compounds increases slightly as molecular weight increases. Other factors can play a role in this as well (e.g., filler level and type, and degree of fusion). Outdoor weathering may see a slight boost with higher-molecular-weight resins for the reasons noted in Section 2.3.1.4. Resistance

TABLE 2.2 Effect of Resin Molecular Weight on Properties of Compounded PVC Homopolymers

IV	HDT at 66 psi	Abrasion % Weight Loss, 2000 Cycles	Tensile Strength (psi)
1.02	74	0.03	8000
0.93	74	0.03	8100
0.52	70	0.18	4800

Source: *Handbook of PVC Formulation*, 1st edn, Wiley Interscience, 1993, p. 50.

to abrasion, tear, creep, deformation at elevated temperatures, and flex fatigue resistance increases with increased molecular weight (Table 2.2). Surface gloss tends to decrease with increasing molecular weight; however, process conditions play a role in this as well.

Like flexible PVC compounds, the resins used in rigid PVC must be properly fused in order to achieve optimal physical properties. Although fusion is important in flexible PVC applications, proper compound fusion is even more critical for rigid PVC applications.

2.4.2 Manufacturing Processes

2.4.2.1 Fusion Properties The fusion properties of rigid PVC resin depend primarily on molecular weight: the higher the molecular weight, the slower the fusion. This is illustrated in Fig. 2.3. There are other factors that can also affect fusion. Resin particle size distribution and resin bulk density will also have an effect on fusion. The more tightly the resin particles are packed, the more efficiently heat and mechanical energy are transferred from the screw and barrel to the resin. This phenomenon is described in greater detail in Section 2.7.1.

Another factor affecting resin fusion characteristics is the presence (or lack) of an antistatic surface treatment on the resin particle surface. Some resin manufacturers use calcium stearate as an antistatic agent at levels ranging from 0.1 to 0.2 percent. Calcium stearate is one of the main additives used to speed fusion in rigid PVC compounds. Therefore, the presence of calcium stearate on the resin particle surface will

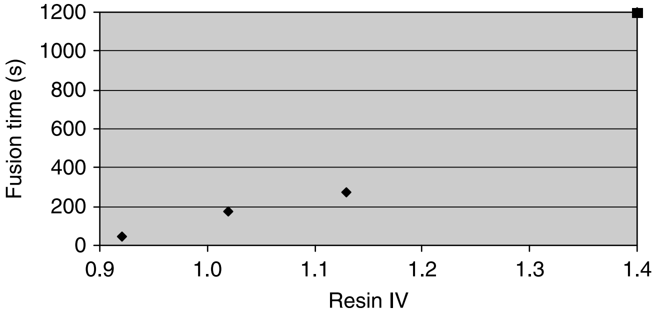

Figure 2.3 Effect of molecular weight on fusion time on rigid PVC formulation at 174 °C.

have a tendency to speed fusion. This effect becomes more noticeable in pipe and other formulations where low levels of calcium stearate are traditionally used.

2.4.2.2 Melt Viscosity The melt viscosity of rigid PVC formulations increases as resin molecular weight increases. This is a major issue in rigid PVC formulations, since the polymer melt viscosity is usually much higher in rigid PVC formulations than in flexible PVC formulations. Although higher-molecular-weight resins yield physical property benefits in rigid PVC, they tend to be much more difficult to process and often create issues with melt pressure, high extruder amp draw, and thermal stabilization due to increased levels of shear.

2.4.2.3 Melt Strength Higher-molecular-weight resins, when properly fused, will yield increased melt strength versus lower-molecular-weight resins. Melt strength in rigid PVC formulations can also be improved through the use of process aids and lubricant selection.

2.4.2.4 Die Swell As with flexible PVC formulations, as the molecular weight of the PVC resin increases, die swell tends to decrease. Decreases in process melt temperature and shear rate will also yield a decrease in die swell.[19] The die swell characteristics of rigid PVC formulations are also dependent on process aid type and level, impact modifier type and level, filler type and level, and compound lubrication.

2.5 EFFECT OF RESIN SELECTION ON PLASTISOL PHYSICAL PROPERTIES AND MANUFACTURING PROCESSES

2.5.1 Physical Properties

The effect of resin molecular weight on the physical properties of plastisol compositions is the same as for flexible PVC. The incorporation of blending resin or copolymer resin into a plastisol formulation will generally decrease physical properties versus plastisol formulations based entirely on dispersion resin of the same molecular weight.

2.5.2 Manufacturing Processes

2.5.2.1 Air Release The air release properties of a dispersion PVC resin are governed by both the formulation and the surface coating on the plastisol resin. Air release is facilitated by low plastisol viscosity at low shear rates and a reduced surface tension. Coatings on the dispersion resin particle surface can have a significant effect on viscosity and surface tension, as can other additives. Resin particle size can also play a role in air release, with larger particle sizes yielding improved air release.

2.5.2.2 Viscosity The viscosity characteristics of a plastisol are affected by both the resin surface coating and the particle size distribution of the resin(s) in the system.

Generally, as the level of a given surface coating increases on the resin particle surface, the plastisol viscosity decreases. Small resin particles with a narrow unimodal particle size distribution will also yield higher viscosities than will resin particles with a broad unimodal or multimodal distribution. This is one of the reasons that larger-particle-size blending resins are often used in conjunction with smaller-particle-size dispersion resins to reduce plastisol viscosity.

2.5.2.3 Fusion Properties As with both flexible and rigid PVC, the higher the resin molecular weight, the slower the fusion. Plasticizer selection also plays a major role in plastisol fusion properties. PVC/vinyl acetate and other copolymer resin systems are sometimes used to speed fusion in plastisol systems. As the copolymer content increases, the rate of fusion increases.

2.5.2.4 Water Absorption The water absorption characteristics of plastisols are of critical importance. The inclusion of water into the plastisol matrix can lead to blistering in the final product. Although calcium oxide is effective at reacting with the available water, proper resin selection can reduce the tendency of a plastisol to pick up water during processing and storage. The most important resin-related factor for water absorption is surfactant level. The surfactants normally remaining on the dispersion resin particle surface were originally designed to keep the resin particle suspended in water. Therefore, these surfactants tend to have an affinity to water. Using resins with lower surfactant levels will often yield reductions in water absorption.

2.6 RESIN SELECTION FOR SPECIFIC FLEXIBLE PVC APPLICATIONS

2.6.1 Wire and Cable

2.6.1.1 General Purpose Jackets Most general purpose jacket compounds use resins with a K-value around 70. Normally, these formulations range from 60 to 90 Shore A (15 s dwell) in hardness and have specific gravities ranging from 1.30 to 1.50 g/cm^3. These types of formulations can be easily processed on most single-screw extruders. Because of this, there is no need to modify resin molecular weight for most general purpose jacket applications.

2.6.1.2 Specialty Jackets Jacket formulations requiring improved abrasion, tear, or plasticizer migration resistance can benefit from the use of higher-molecular-weight resins. Gloss reductions can be achieved through the use of either high-molecular-weight resins or blends of partially crosslinked PVC resin with homopolymer resin. Lower-molecular-weight resins can improve output on some processing equipment, but lead to reductions in most physical properties. Low-temperature properties can be improved through the use of higher-molecular-weight resins. In applications requiring the use of polymeric plasticizers or high levels of monomeric plasticizers, high-porosity PVC resins are sometimes employed to speed dry time and improve the handling properties of these compounds in powder or pellet form. High-molecular-weight resins are also useful in these applications due to their ability to hold higher levels of plasticizer, thus reducing surface tackiness and plasticizer exudation on the finished product over time.

2.6.1.3 Insulation Applications Resin electrical properties become critical for insulation applications (the compound in direct contact with the metal conductor). Resins need to be specially manufactured in order to minimize residual initiators, catalysts, and contaminants, which can negatively impact electrical properties. One of the ways this is accomplished is by carrying out the suspension resin polymerization process in deionized water and minimizing residual surfactant.[12] Mass resins have found use in this application in the past due to the fact they do not require electrically deleterious surfactants agents in their manufacture. In order to minimize raw material inventory, many wire and cable manufacturers who compound their own PVC formulations attempt to use the same resin for both jacket and insulation compounds. Because of this, resins with a K-value around 70 also predominate in insulation applications.

Many of the high-volume insulation formulations used in wire and cable have durometers over 85 Shore A (15 s dwell) and are extruded onto wire at speeds that can exceed 2000 m/min. Some wire and cable manufacturers have found that by using resins with K-values between 66 and 68, they can increase their extrusion rate. There are two primary mechanisms for the rate increase.

By reducing the molecular weight of the resin, one also reduces the formulation's melt viscosity, thus often yielding an increase in output. The other reason for line speed improvements involve the crystallite regions present in the PVC resin. As a rule, the crystallites in lower-molecular-weight PVC tend to melt at lower temperatures than those of higher-molecular-weight PVC resins. Therefore, at any given extrusion temperature, lower-molecular-weight PVC resins normally have fewer remaining crystallites than higher-molecular-weight resins. Eliminating as much of the crystallite phase as possible will result in improved extrusion characteristics under high-shear environments, thus permitting the compound to be processed at faster rates through the high-shear conditions encountered in wire and cable insulation extrusion.[20]

2.6.1.4 Flame-Retardant Applications The reason PVC has such a strong position in wire and cable applications is its inherent flame resistance. In addition to combustion inhibition in the flame front due to the presence of chlorine in the polymer, PVC also forms a stronger char than most other nonhalogenated polymers due to the formation of hydrogen chloride during degradation. Higher-molecular-weight polymers tend to form stronger chars and are less likely to drip during combustion than lower-molecular-weight resins.

Other factors affect resin selection for flame-retardant applications. PVC is often compounded with other additives to improve flame and smoke properties. Flame-retardant loadings exceeding 50 phr are not uncommon in riser jacketing applications and are the rule in plenum jacketing applications. Lower-molecular-weight resins can improve both output and process thermal stability in some of these formulations. Unfortunately, these highly flame-retarded PVC formulations tend to push the limits on UL (Underwriters Laboratories) physical property requirements for flame-retardant cable applications. Because of this, lower-molecular-weight resins may not be an option in some cases.

Aluminum trihydrate (ATH) is one of the most common flame-retardant additives used in PVC. ATH functions by releasing its waters of hydration at temperatures around 200 °C and above.[21] Under high-shear conditions, the melt temperatures of highly filled ATH containing flame-retardant compounds can rise high enough during extrusion to liberate some of the ATH's waters of hydration during processing. Although "foaming" a compound can lead to significant product cost savings, UL inspectors as well as customers tend to disapprove of this practice.

One way to reduce the chances of releasing these waters of hydration during processing is to lower the molecular weight of the PVC resin. This, in turn, will reduce the shear encountered during processing. The reduced shear then results in a lower melt temperature, which then reduces (or eliminates) the potential of liberating water from the ATH during processing.

2.6.2 General Purpose Flexible Profile Extrusion

Resin selection for general purpose extrusion applications is dependent on many factors. Some of these factors are finished product physical properties, compound flow properties inside the extrusion die, die swell properties, and compound melt strength.

The compound flow characteristics inside a extrusion die are normally controlled through the use of plasticizers, fillers, and lubricants. However, there are some situations where resin selection may be the best way to modify compound flow characteristics inside of and immediately exiting the die. Lower-molecular-weight resins will yield better flow characteristics at any given temperature than high-molecular weight resins and often do a better job of "filling out" die legs. Also, if the die design has sharp edges in flow regions or has areas of restricted flow, reducing the molecular weight of the resin may help reduce degradation in these areas, thus lengthening extrusion run time and improving product quality. The main drawbacks to reducing the molecular weight of the resin are a reduction in physical properties and melt strength and an increase in die swell.

Compound melt strength is enhanced as resin molecular weight increases. Having a strong compound melt enables the extrusion compound to better retain the profile shape after exiting the die prior to cooling. Also, a strong compound melt can enable the processor to increase compound "draw down". By carefully controlling the manufacturing process, the processor can have compound exiting a large die (less flow restriction) at perhaps 50 m/min while the take-up lines are running at 100 m/min. If the profile is conducive to drawdown, the processor can take advantage of this effect to increase line speed. There is a potential danger with high drawdown ratios. If the profile is cooled too quickly before the polymer chains can fully relax, stress can be "frozen" into the profile. This stress can relax over time or during exposure to elevated temperatures, potentially causing shrinkage or deformation in the finished part.[22]

2.6.3 Non-Plastisol Flooring Applications

2.6.3.1 Vinyl Composition Tile When customers wanted lower-cost alternatives to marble floors, vinyl formulators may have taken their request too literally. Vinyl composition tile (VCT) formulations typically contain over 80 percent calcium carbonate by weight. Because of the extremely high filler loadings in these products, resin selection is critical for these applications.

The main issue encountered by VCT manufacturers is fusion. Trying to fuse PVC formulations with over 700 phr of calcium carbonate is a challenge few PVC processors ever have to face. Because of this, lower-molecular-weight homopolymer resins with K-values ranging from 55 to 59 predominate in these applications. The fusion challenges of VCT tend to make the Banbury the preferred mixer for these compounds.

In addition to containing lower-molecular-weight homopolymer resins, PVC/vinyl acetate copolymer resins are normally used in these applications to speed fusion. The copolymer resins used in VCT normally have copolymer contents ranging from 10 to 15 percent and K-values ranging from 50 to 60. There resins are discussed in greater detail in Section 2.8.3.1. There is no single optimum ratio of homopolymer resin to copolymer resin: the optimum ratio is dependent on raw material cost, mixing equipment, and downstream calendering equipment.

Since PVC/vinyl acetate copolymer resins are more expensive than PVC homopolymer resins, the tendency is to try to maximize the homopolymer resin content. One way this can be done is through the use of fast fusing plasticizers such as butyl benzyl phthalates. Since the pricing of PVC/vinyl acetate copolymer resins and butyl benzyl phthalate plasticizers varies independently over time, the optimum ratio of homopolymer to copolymer resin for a given product or manufacturing process can change over time and should be re-evaluated periodically. Another consideration when using PVC/vinyl acetate copolymer resins is their negative effect on compound stability. Specially formulated heat stabilizer systems can help reduce or eliminate this problem.

Although many PVC processors have difficulty using resins with high gel levels, VCT manufacturers often use off-spec resins with high gel and contamination levels. This is because VCT formulations containing 80% calcium carbonate by weight generate a great deal of shear during the manufacturing process. These high levels of shear can obliterate most if not all resin gels. Even if a few resin gels survive the manufacturing process, the surface quality requirements of VCT products tend to be much lower than those for other PVC-based consumer products. VCT applications are also more tolerant of non-PVC-based contaminants in the resin than most other vinyl applications. Another point to note is that VCT tile formulations often provide a home for a wide variety of PVC- and non-PVC-based scrap.

Since most VCT is manufactured by a calendering process, the ability to maintain hot melt strength is important. Asbestos was used to improve the hot melt strength of vinyl asbestos (VA) tile, the predecessor of VCT, until a link was established between asbestos and a rare form of lung cancer called mesothelioma. The subsequent litigation wreaked havoc on the flooring manufacturers who previously manufactured VA tile. The melt strength of VCT is generally improved by increasing resin molecular weight or decreasing vinyl acetate copolymer content. Another important factor is the degree of compound fusion. If the compound is not well fused, it will have difficulty surviving downstream calendering processes.

Once the VCT is formed into a sheet and cut to size, it has to meet certain physical property requirements. Although the extremely high filler loadings in VCT lend good dimensional stability characteristics to the finished product, product made with "frozen-in" stress can undergo dimensional changes, especially at elevated temperatures. Therefore, it is desirable to minimize the recoverable strains introduced into the calendered sheet during processing.[23] Dimensional changes can also be caused by water absorption. Although water absorption is formulation-dependent, insufficiently fused VCT products can have issues with water absorption. Resin changes to improve fusion characteristics can sometimes help to resolve these types of issues.

Impact and abrasion resistance are two other characteristics commonly measured in VCT products. Both characteristics are improved with higher-molecular-weight homopolymer and copolymer resins. The vinyl acetate present in copolymer resins tends to be a detriment in these areas. Once again, poorly fused products will nullify any potential improvements in impact and abrasion resistance due to increases in resin molecular weight.

2.6.3.2 Solid Vinyl Tile Solid vinyl tile is considered a premium flooring product when compared with vinyl composition tile. It was originally developed as an alternative to rubber tile products, but now also competes with VCT in mid- to high-end applications. Solid vinyl tile has significantly better physical properties than VCT and generally has a wider range of color and styling options. The improved physical properties are achieved principally through two means: reduced filler levels and higher-molecular-weight resins. Homopolymer resins with K-values ranging from 59 to 66 are generally used in these applications.[24] Due to the reduced filler levels versus VCT, solid vinyl tile applications usually do not require PVC/vinyl acetate copolymers to aid fusion.

2.6.3.3 Cove Base Cove base (also referred to as "wall base") is the flexible PVC-based transition product between the floor and wall in many commercial environments. The major physical property requirements for this product is the ability to bend around 90° corners without cracking and not to experience shrinkage over time after installation. Although cove base might not crack initially when installed, cracks and splits can occur over time, especially if the cove base is repeatedly struck on a 90° corner.

Although cove base dies are fairly large and simple when compared with other flexible extruded PVC products, the high filler levels normally present in these products can create viscosity issues. Because of this, resins with K-values around 66 tend to be used. Some cove base products are co-extruded. In these cases, there are more options with capstock resin and substrate resin selection based on formulation, tooling, and manufacturing process decisions. The substrate of co-extruded cove base products also makes a good home for flexible PVC scrap.

2.6.4 Resin Selection for Flexible Film and Sheet

2.6.4.1 Resin Selection Issues Common to Both Extruded and Calendered Sheet

2.6.4.1.1 Resin Gel Content Although the resin requirements for extruded film and sheet are similar to those of other general purpose extrusion applications, some differences exist. Resin gel content (or lack thereof) is extremely important for extruded film and sheet. Since suspension resins typically have lower gel levels than mass resins, suspension resins are generally preferred in these applications. The two main ways resin manufacturers control gel content are through resin reactor hygiene and resin porosity.

At one time, PVC reactors tended to be about 6–7 ft in diameter. This was done to make it easy for workers to clean the reactors. Cleaning was necessary since PVC resin deposits would begin to form in spots along the reactor walls after a few batches. If left unchecked, this "scale" created nucleation sites for large resin particles to grow during polymerization. These large particles would then intermittently break off of the reactor walls and create gel issues in the final product.

Today, PVC reactors range up to 10,000 gallons in size. Since these new, larger reactors are much harder to clean by hand than the older reactors, "clean reactor" technologies were developed to minimize the scale formation on the sides of the reactor. The other benefit to this technology is that it reduces worker exposure to vinyl chloride monomer.[12] Now, it is common for reactors to make several hundred batches of PVC resin between cleanouts.[25]

Often, film-grade resins are virtually identical to normal extrusion-grade resins. The key is that the first batches of resin from a newly cleaned reactor are normally designated as "film grade." Resin from later batches would then be designated as "extrusion grade." The point where the resin designation changes from film grade to extrusion grade is flexible and is often more dependent on resin product demand than a fixed number of batches after a cleanout.

Higher levels of resin porosity also tend to reduce gel levels in the final product. The more porosity a resin particle has, the more easily it can absorb plasticizer and fuse with the other resin particles. The correlation is not perfect, but there is a strong relationship between gel content and porosity in resins for flexible PVC applications.

2.6.4.1.2 Clarity Clarity is an issue in many extruded film or sheet applications. One can often find clarity differences in PVC resins that would appear to have similar properties at first glance. Many PVC resins sold into extruded film and sheet applications contain antistatic treatments as well as residual materials from the polymerization process. These treatments and contaminants have an effect on product clarity.

Calcium stearate, a common resin antistatic surface treatment, is known to have a negative effect on clarity.

Interestingly enough, resin molecular weight can also have an effect on clarity. One of the keys to having good clarity in the finished product is to have good fusion. Lower-molecular-weight resins are easier to fuse than higher-molecular-weight resins. Therefore, lower-molecular-weight resins sometimes demonstrate higher levels of clarity, depending on the manufacturing process. Of course, acrylic processing aids with refractive indices close to that of PVC, and fast-fusing plasticizers such as benzyl phthalates can also aid fusion and therefore improve clarity.

Another PVC resin quality issue that can cause problems in clear film and sheet applications is the presence of dark resin particles in the finished product. After mechanically removing water from the freshly polymerized suspension PVC resin particles, the resin is dried further by heat. PVC resin manufacturers have figured out that the higher the drying temperature, the faster they can dry the resin. If the resin drying process is too aggressive, or if there are regions in the drying process where resin particles can "hang up," dark or degraded resin particles can be produced.

2.6.4.1.3 Printability Much of the flexible film and sheet produced undergoes printing. Although additive selection is critical in determining the printability of a formulation, resin selection can play a role. For example, a semirigid PVC film or sheet formulation containing 25 phr of plasticizer is generally easier to print after storage than the same formulation containing 50 phr of plasticizer. Unfortunately, the semirigid formulation will normally require hotter calender rolls than the more flexible formulation. In a situation like this, moving to a lower-molecular-weight PVC resin may permit the processing of semirigid formulations on equipment that cannot achieve the temperatures required to process semirigid formulations based on higher-molecular-weight resins. This, in turn, can yield improvements in retained printability due to a reduction in plasticizer level. The use of vinyl acetate copolymer resins can also yield improvements in printability.

2.6.4.1.4 Miscellaneous Properties Tear and puncture resistance is improved with higher-molecular-weight resins. Higher-molecular-weight resins are also useful in applications where high melt strength is required or other downstream operations necessitate a tougher product. Higher-molecular-weight resins also find use in applications where higher plasticizer levels are used or where improved physical properties are required.

2.6.4.2 Extruded Flexible Film and Sheet The resin viscosities used in extruded film and sheet are dependent on the application, but normally K-values range from 60 to 71, with 66 being an "average" viscosity. Although resin gel content is critical in many extruded and calendered flexible film and sheet applications, extruded products are less tolerant to gels as a rule than calendered products. Since one can achieve sheet products of greater thickness with the extrusion process, differences in clarity between resins can become more important.

Surface gloss is often important in extruded film and sheet products. It is a function of both process conditions and resin molecular weight. Generally, higher processing temperatures and/or lower-molecular-weight resins will yield an increase in surface gloss. An old trick to improve gloss in sheet applications is to blend dispersion resin with regular PVC homopolymer resin. It is believed that the surfactants commonly used to coat the dispersion resin particles act as PVC lubricants and enhance gloss on the finished product. The drawback to using dispersion resins in this application is the issues they can cause with printability. In most cases, this reduction in printability is due to the same surfactants that are believed to improve gloss.

If reductions in gloss are desired, crosslinked PVC resins can be blended with homopolymer resins. In order to maximize gloss reduction, the apparent viscosity of the crosslinked resin should be higher than that of the homopolymer resin it is being blended with.

2.6.4.3 Calendered Flexible Film and Sheet Many of the requirements listed above in Section 2.6.4.2 apply to calendered film and sheet as well. There are a few differences, which are highlighted below.

Lower-molecular-weight resins require lower calender heats and can be used in applications where physical properties are not critical. They also offer benefits in applications where formulation additives (i.e., polymeric plasticizers) cause roll sticking problems at elevated temperatures.[26] They also have benefits when the calender rolls have trouble achieving sufficiently high temperatures to process higher-molecular-weight resins.

Desired surface gloss levels, whether high or low, can often be obtained through the use of “polishing” or “embossing” rolls on a calender line. Because of this, some of the gloss control obtained through resin specification on extruded products may not be needed for calendered products. However, many of the formulation-related gloss control techniques used in flexible PVC extrusion will also work in calendered fim and sheet applications.

Although resin gels are never desirable, opaque calendered film and sheet is normally less susceptable to gel-related surface defects than extruded film of the same thickness. However, as the thickness of the calendered film decreases, gel issues become more important. If the film is thin enough, gels can cause pinholes in the final product. Resin gels can occasionally cause pinholes in flexible sheet applications as well, especially in applications where the sheet undergoes a subsequent thermoforming process. As always, gels, black resin particles, and other resin contamination issues can cause major problems in clear calendered film and sheet applications.

2.6.5 Flexible Injection Molding

Flexible PVC is normally much easier to injection-mold than its rigid counterpart. Since plasticizers have a dramatic effect in reducing flexible PVC melt viscosity, many compounds originally developed for extrusion applications can be injection molded as well. Although resins with *K*-values of 70 or higher are sometimes used in flexible injection molding applications, resins with *K*-values ranging from 65 to 68 predominate. PVC resins with even lower molecular weights can be useful when trying to mold complex shapes, when using molds with poorly designed gates and runners, or when trying to mold high-durometer compounds.

Injection molding compounds based on lower-molecular-weight resins also tend to develop less shear heating and can be molded at lower temperatures than compounds based on higher-molecular-weight resins. The reduced heat buildup during the injection molding process can lead to faster cycle times and reduced stabilizer demand. Reduced stabilizer demand can help increase the amount of regrind that one can incorporate into the molding process.

2.6.6 Flexible Blow Molding

Many of the resin selection requirements for flexible injection molding also apply for flexible blow molding as well. However, resins with *K*-values as low as 60 can be found in semirigid blow molding applications. Compound melt viscosity and melt strength can be adjusted by changes in plasticizer level and process conditions; however, altering the resin molecular weight is sometimes the preferred way to adjust these compound characteristics. Resin *K*-values for flexible injection blow molding applications tend to be lower than those used for extrusion blow molding applications.

2.7 RESIN SELECTION FOR SPECIFIC RIGID PVC APPLICATIONS

2.7.1 Pipe

2.7.1.1 Resin Selection Issues Common to Most High-Volume Pipe Applications Pipe is the largest product application area for PVC resin and is definitely one of its most competitive applications. In order to keep cost to a minimum, the major producers extrude rigid PVC powder compound and are highly focused on minimizing cost and maximizing product output. We will first discuss PVC resin concepts important to all three major types of PVC pipe: pressure pipe, DWV (drain waste and vent) pipe, and sewer/drainage pipe. After covering the PVC resin requirements that each have in common, we will then cover each type of pipe product individually.

2.7.1.1.1 Resin Bulk Density There are several resin characteristics to which pipe producers pay great attention. The first characteristic is the bulk density of the resin. This is important because as resin bulk density increases more compound can occupy the feed section of the extruder. As the amount of compound in the feed section increases, the potential output under a given set of process temperature increases.

One of the factors affecting resin bulk density is static charge buildup on the resin particles. When the resin particles build up static charge, they tend to repel each other, thus decreasing the resin bulk density. Through the use of resin surface treatments and carefully controlled resin drying procedures, the resin particles will contain low levels of moisture. This controlled level of moisture on the resin particle surface will help dissipate static charges that can build up during resin transfer operations.

2.7.1.1.2 Resin Porosity Resin porosity is a desirable characteristic for flexible PVC. In rigid PVC, a small amount of porosity is desirable to facilitate the absorption of the liquid stabilizer and other lubricants. However, excessive resin porosity can be a detriment to rigid PVC by lowering the bulk density of the resin. As mentioned above, this can have a negative effect on extruder output.

2.7.1.1.3 Resin Particle Size Distribution Resin particle size distribution is also important in achieving higher resin bulk densities. By adjusting the packing fraction of the resin particles, one can get more PVC polymer into a given space, thus enhancing the resin bulk density. Another reason why resin particle size distribution is important is that it influences the fusion characteristics of the compound. Usually, pipe producers want to see particle size distribution consistency from lot to lot, thus enhancing fusion consistency.

If the fusion characteristics of the resin stay consistent, output stays consistent. This is extremely important to a pipe producer. The objective of a pipe producer is to run as close to the product dimensional tolerances as possible. If the resin particle size or bulk density changes during extrusion, there will be inconsistency in product output. In order to compensate for this, the pipe producer may have to run slightly oversize on pipe dimensions in order to compensate for fusion-related output differences and to consistently meet minimum dimensional requirements. If a pipe producer must manufacture products an average of 2 percent overweight due to fusion-related output inconsistencies and the pipe producer consumes 50 million pounds of PVC compound in one year, the pipe manufacturer is arguably shipping one million pounds of free compound to customers each year.

The ideal situation for pipe producers is to run their extruders for weeks at a time without having to shut down or make process changes. This type of situation tends to produce low product scrap rates. Consistent resin particle size and resin bulk density are important in achieving these goals.

2.7.1.2 Pressure Pipe Solid pressure pipe made with type I rigid PVC compounds have tightly controlled physical property requirements. Even though pipe manufacturers tend to be quite secretive about their formulations, these physical property requirements tend to yield formulations of amazing similarity. Due to burst strength requirements, it is difficult to make pipe cost effectively with resin with a K-value below 65.[27] Usually National Sanitation Foundation (NSF)-approved PVC resin with a K-value of 65 or 66 predominates in these applications.

Since PVC pressure pipe manufacturers can meet their physical property requirements with a resin of K-value 66, there is little benefit to going to a higher-molecular-weight resin. There tends to be little need to alter the compound's flow characteristics due to the relative simplicity of the pipe die when compared with other rigid PVC profile dies. Since the die design is circular, the pipe dimensions can be fine-tuned by the calibrator or by changes in extruder output and downstream take-up.

2.7.1.3 Drain, Waste, and Vent Pipe Like solid pressure pipe, drain, waste, and vent (DWV) pipe has tightly controlled physical property requirements that tend to favor the use of resin with a K-value of 65–66. The main formulation difference between pressure pipe and DWV pipe is that higher filler loadings are usually possible with DWV pipe products.

2.7.1.4 Sewer/Drainage Pipe When compared with pressure and DWV pipe, sewer pipe and drainage pipe are not as heavily regulated. Because of this, some latitude in resin selection is possible due to the lower physical property requirements of sewer and drainage pipe products. Lower cost off-spec non-NSF-approved resins can be used in these applications, enabling some cost reduction opportunities. Interestingly enough, resin pricing can become an important factor in sewer and drainage pipe resin and filler selection.

When PVC resin prices are high, the economics favor high levels of the more expensive fine particle size (1 μm or less) calcium carbonates. This approach tends to increase melt viscosity, so the use of lower-molecular-weight resins to reduce melt viscosity may have benefits in some cases. When PVC resin prices are low, the economics favor the use of larger particle size (3 μm or greater) calcium carbonate at lower use levels in conjunction with the typical pipe resins of K-value 65–66 used for pressure pipe. The employment of low-cost large-particle size fillers at reduced use levels tends to negate the advantages of reduced melt viscosity offered by the more expensive lower-molecular-weight resins.

Foam core pipe now dominates the larger-diameter sewer and drainage pipe market and is moving into smaller-diameter products. As the name implies, the pipe core is foamed to reduce the amount of compound used to make the pipe while maintaining the necessary physical properties for the application. These products are co-extruded, which requires a higher capital outlay initially. However, the material cost savings quickly justify the increased capital and compound expense in most situations. End users have also grown to like the reduced weight and the ease of cutting of foam core pipe products.

The exterior surface of the foam core pipe generaly uses a resin K-value somewhere around 65–66. There are benefits to using lower-molecular-weight resins in rigid PVC foam applications; however, most pipe manufacturers use a resin of the same molecular weight for the foam core as they do for the capstock to maximize their resin usage and minimize resin inventory. Also, the higher-molecular-weight resins yield better mechanical properties. Most foam core formulations contain higher levels of process aid in order to improve fusion and facilitate foaming. Sewer and drainage pipe also make an excellent home for rigid PVC pipe scrap.

2.7.2 Resin Selection for Siding Applications

Most PVC siding products are co-extruded. The capstock tends to be lightly filled or sometimes unfilled with good impact properties and weatherability, while the substrate tends to be more highly filled to reduce overall product cost.

2.7.2.1 Capstock Although the capstock normally ranges from 0.003 to 0.008 in and usually comprises 20 percent or less of the finished siding product's thickness, it is the most critical part of the product.[28] This is the region of the construction that requires good impact and weathering properties. The impact properties are achieved through a combination of impact modifier and resin selection. As stated before, higher-molecular-weight resins yield better impact properties and are preferred in capstock applications. With higher-molecular-weight resins, one can use less impact modifier in the formulation, thus reducing formulation cost. The impact resistance benefits of higher-molecular-weight resins are especially noticeable at low temperatures—an environment much of the vinyl siding sold in North America unfortunately experiences. Another factor is the thickness of the capstock. Generally, the thicker the capstock, the better the impact resistance of the overall construction.

In the early 1990s, most resin capstock was made using resin with a K-value of 65–66. Today, some siding capstocks now use resin with a K-value of 68, and higher-molecular-weight resins are being explored. Although the melt viscosity of these resins is higher, the use of Fischer–Tropsch waxes and other linear waxes based on alpha-olefins has made it possible for many fabricators to process these higher-molecular-weight resins on existing equipment.[29]

Gloss is another factor that enters into the resin selection equation. The present styling trends for siding trend towards low gloss levels. This can be achieved through reduced process aid levels, crosslinked PVC resin, ethylene vinyl acetate copolymers with VA contents $<45\%$, and special impact modifiers. However, increased resin molecular weight can also yield reduced gloss effect in capstock. One must be careful in the quest for reduced gloss, many of the additives or manufacturing process changes that reduce surface gloss in extruded products can have a negative effect on impact properties.

In order for the capstock to function well, it must exhibit good adhesion to the substrate. There are many formulating and processing factors that play a role in this adhesion, one of which is resin molecular weight. The lower the resin molecular weight, the easier it is to get good adhesion. Of course, compound lubricant selection plays a major role in capstock/substrate adhesion, with paraffin waxes being notorious for causing problems in this area. Also, resin gels are a concern. The typical low-cost pipe grade resins often have too many gels for most siding capstock applications.

2.7.2.2 Substrate The resin selection criteria for substrate is less critical and is dependent on the formulation choices made for the capstock, the thickness of the capstock, and the impact properties required for the final product. One of the major differences between capstock and substrate resin requirements is that the substrate can tolerate higher levels of gels and contaminants since its surface is not exposed. Since the substrate can comprise 80 percent or more of the siding product, significant cost savings can be achieved through the use of lower-cost pipe grade resins with *K*-values of 65–66.

Another potential benefit to examining the use of lower-molecular-weight resins in the substrate is improved adhesion of the capstock to the substrate. A strongly bonded interface is more effective at transferring energy from an impact at the capstock surface through the substrate. Energy dissipation is one of the keys to maintaining the integrity of the capstock after impact.

2.7.3 Other Extruded Rigid PVC Products

Co-extruded products for exterior applications such as PVC fencing or window profile generally follow the same resin selection guidelines given for PVC siding. For exterior profile applications that are not co-extruded, many of the resin selection guidelines given for siding capstock apply. However, the wide variety of die designs found in window profile and other exterior extrusion applications often necessitate changes in PVC resin molecular weight in order to achieve the necessary compound flow and die swell characteristics. Most rigid PVC extrusion compounds for exterior applications have *K*-values ranging from 64 to 71,[15] with values of 65–68 predominating. However, the author is aware of numerous exterior rigid PVC extrusion compounds with PVC resin *K*-values below 64.

Interior products tend to have more options in terms of resin selection. Impact resistance for interior products tends to be less of an issue than for exterior products. In these cases, lower-molecular-weight resins can be used to facilitate easier extrusion. Also, interior products tend to be more highly filled than exterior products, which can also have a significant effect on resin selection.

2.7.4 Rigid PVC Foam

Resin selection is extremely important for rigid PVC foam applications. The key to obtaining the greatest degree of foaming in conjunction with good cell structure is to ensure that the resin is well fused during the decomposition of the blowing agents. High-molecular-weight process aids are useful in helping to achieve this but lower-molecular-weight resins are key in this endeavor. PVC homopolymer resins with *K*-values ranging from 57 to 62 are generally preferred for these applications. The lower-molecular-weight resins fuse at lower temperatures than their high-molecular-weight counterparts and therefore exhibit better melt elasticity at lower temperatures. When the resin exhibits good melt elasticity, the cell walls will retain their integrity during expansion. The reason why the resin should fuse at relatively low temperatures is that sufficient melt elasticity needs to be in place before too much of the blowing agent decomposes. If the blowing agent decomposes before good melt elasticity is achieved, the result is usually collapsed cells and higher product densities.[30]

However, higher-molecular-weight resins tend to yield compounds with better physical properties. Many rigid PVC foam profiles are nailed or mechanically fastened to another part or surface. Properly fused resins with *K*-values 65 or higher are sometimes used in these applications because they are less likely to split or incur damage when nailed, cut, or mechanically fastened than the lower-molecular-weight resins typically used in foam applications.[29]

2.7.5 Rigid PVC Extruded Film and Sheet/Calendered Sheet and Film

The end use application is critical for resin selection. If the sheet is to be thermoformed, the resins selected will tend to be in the lower end of the molecular weight ranges specified below for these applications. PVC/vinyl acetate copolymers or sometimes ABS resins are blended with the homopolymer resin to improve the ability of the formulation to undergo deep draws in the thermoforming operation. PVC/vinyl acetate copolymers also find use in applications where printability of the sheet is critical. In applications where clarity is important, lower-molecular-weight resins tend to do better than higher-molecular-weight resins due to improved fusion characteristics. However, clarity differences often exist between resins of the same molecular weight. Products with thicknesses exceeding 0.010 in (0.254 mm) are generally referred to as sheet, while products with thicknesses below 0.010 in (0.254 mm) are generally referred to as film.[31]

2.7.5.1 Extruded Film and Sheet One of the benefits to extruding rigid PVC film/sheet is that capital investment costs are usually lower and that a wider range of sheet thicknesses are possible. The extrusion process is also better suited for shorter production runs, although calenderettes sometimes compete with the extrusion process in these applications. Extruded film and sheet is extremely sensitive to gels and other particulate contamination, so resins with low gel content are critical in many extruded sheet applications. The resins used normally have *K*-values ranging from 57 to 66. Generally, the thin-gauge products use resins towards the lower end of the *K*-value range noted above in order to minimize melt viscosity. Thicker-gauge products, due to decreased levels of shear at the die, can often take advantage of the physical property benefits of higher-molecular-weight resins.

2.7.5.2 Calendered Film and Sheet The calendering process tends to have cost benefits over the extrusion process in high-volume applications. Most rigid PVC calendered film and sheet is processed in thicknesses ranging from 0.004 to 0.030 in (0.101 to 0.762 mm), while oriented sheet calenders can process films down to 0.001 in (0.025 mm). Rigid PVC calendered sheet generally uses suspension resins with *K*-values ranging from 55 to 62.[26] Calendered film and sheet is less sensitive to resin gels than film and sheet manufactured by the extrusion process, but resins with low gel contents are still the norm. As with extruded sheet, lower-*K*-value resins have benefits in high-shear thin-gauge applications.

2.7.6 Rigid PVC Injection Molding

Rigid PVC injection molding is a far more difficult process than flexible PVC injection molding. The main issue is the comparatively high melt viscosity of rigid PVC versus that of flexible PVC. Because of this, resins used in rigid PVC injection molding compounds tend to be of much lower molecular weight than the resins used in their flexible PVC counterparts.

2.7.6.1 Pipe Fittings In the United States, the single largest rigid PVC injection molding application is for pipe fittings. Due to the cost-competitive nature of these products and the need to meet certain ASTM (American Society Testing Materials) and NSF requirements, these formulations tend to be similar to one another. Homopolymer resins with K-values ranging from 56 to 58 yield products meeting the physical property requirements and are commonly used in these applications. In applications where impact and burst strength are important, resins with K-values around 60 are sometimes used.

2.7.6.2 Other Injection Molding Applications The general rule for resin selection is that the formulator uses the lowest-molecular-weight resin that he can while still cost effectively meeting physical property requirements. Ultra low-molecular-weight resins (with K-value 52 or lower) are used for difficult to mold parts that do not require high levels of impact resistance. These resins tend to discolor under heat and they shear more readily than their higher-molecular-weight counterparts. This early color development is believed by some to be caused by the chain transfer agents used to keep the resin molecular weight low during the polymerization process.

In molding applications where physical and impact properties are critical, higher-molecular-weight resins are preferred. The same resins used for molding pipe fittings are often the default resins for most rigid PVC injection molding applications. Due to melt viscosity limitations, resins with K-values above 60 are not often used in rigid PVC injection molding applications.

Of course, mold design is a critical factor in resin selection. The runners should be as short as possible and have gradual curves instead of 90° angles. Multiple gates should be used in applications that permit this, and these gates should be as large as possible to minimize shear burning as the compound passes through them. Ideally, shots of longer duration at lower pressure are preferred in order to minimize shear heating. Also, the mold should have sufficient venting to minimize heat buildup caused by compressed air trapped in the mold. The simpler and more streamlined the mold design, the more options the formulator has in terms of resin selection.

2.7.7 Rigid PVC Blow Molding

Typical resins used in rigid PVC blow molding applications have K-values ranging from 55 to 64, with the higher-molecular-weight resins yielding higher melt viscosities and improved melt strength. Resin selection for rigid PVC injection blow molding is similar to that of traditional rigid injection-molded PVC applications.

Rigid PVC extrusion blow molding processes tend to generate less shear than rigid PVC injection molding processes. Therefore, it is possible to use higher-molecular-weight resins in rigid PVC extrusion blow molding applications than one normally encounters in rigid PVC injection molding applications.

2.7.8 Rigid PVC Thermoforming

Like their rigid PVC injection molding counterparts, the resins used in rigid PVC thermoforming formulations tend to be lower in molecular weight. The lower-molecular-weight resins yield a lower-viscosity melt at any given temperature, thus improving deep draw capability. Resins with *K*-values ranging from 58 to 62 are normally used in these applications.[32] As noted previously, blending PVC resin with PVC/vinyl acetate copolymers or with certain grades of acrylonitrile butadiene styrene (ABS) can yield improvements in processability, printability, and surface finish.

Blister pack is one of the most common applications for rigid PVC thermoforming. Since virtually all blister pack is clear, resin clarity is often a criteria for resin selection. Although most blister pack gauge thickness ranges from 0.02 to 0.25 mm (0.0008 to 0.001 in), differences in resin clarity can sometimes be observed in these applications.

2.8 COMMON RESIN TYPES FOR PLASTISOL APPLICATIONS

2.8.1 Dispersion Resin

Plastisol applications are varied and unique when compared to other flexible PVC applications. Often, the most critical formulation critera is not the physical properties of the fused plastisol, but rather the rheological behavior of the plastisol in its unfused liquid state. There are a multitude of ways to control this behavior; one of the best is through resin selection.

As stated before in Section 2.2, plastisol dispersion resins often contain anywhere from 1 to 5 percent residual surfactant by weight. These surfactants are critical in getting the resin to fully disperse in the plastisol. However, they have a major role in the rheological behavior of the plastisol as well as its air release, moisture pickup, and plateout characteristics.

As the plasticizer levels of a plastisol formulation decrease, the resulting viscosity of the plastisol will increase. Higher levels of surfactant on the dispersion resin will normally help to reduce the viscosity of plastisol formulations containing low levels of plasticizer. Another common practice to reduce plastisol viscosity is the use of blending resins.

It should also be noted that plastisol resins have a great deal of variability in terms of heat stability during fusion. It is believed that the level and type of surfactant on the resin particle surface can affect stability due to the potential formation of complexes between the surfactant and mixed metal stabilizer components. These complexes can inhibit the ability of the heat stabilizer to stabilize the PVC polymer, thus possibly yielding premature color formation and polymer degradation during heating. Therefore, one should not assume that dispersion resins in plastisol formulations can be changed without affecting the color development of the fused plastisol.

2.8.2 Blending Resins

Blending resins are normally manufactured by the suspension process and have significantly larger average particle sizes than dispersion resins. This relatively large particle size helps to reduce plastisol viscosity in two ways. The larger-particle-size blending resins have less surface area per unit of mass than the smaller-particle-size dispersion resins. The reduction in total resin particle surface area in formulations containing blending resins yields a reduction in plastisol viscosity.

If all the resin particles are the same size, the plasticizer must occupy the free volume between the resin particles as well as coat the resin particles in order to permit flow. If smaller resin particles are able to occupy much of this free volume instead of the plasticizer, more plasticizer is available to coat the resin particles and aid in flow. Through the use of blending resins, one creates a multimodal particle size distribution, which in turn helps to reduce plastisol viscosity. Depending on the particle size distributions of the blending and dispersion resins, there will be an optimum ratio of blending resin to dispersion resin to yield a minimum viscosity. In most resin systems, the ratio of dispersion resin to blending resin that yields the minimum viscosity typically ranges between 30 : 70 and 70 : 30.[33]

Blending resins do have their drawbacks. First of all, they tend to delay fusion. One of the reasons for this is that the surface area-to-volume ratio of the blending resin is lower than that of the dispersion resin. The second potential issue is reduced physical properties. Although formulation and fusion conditions play a huge role in this, plastisol formulations containing blending resins in general yield poorer physical properties than plastisols based solely on dispersion resins of the same molecular weight. Another significant problem with the use of blending resins in plastisol formulations is that they can settle out of the formulation during storage. Gloss also tends to be reduced in the final product when blending resins are used.

2.8.3 Copolymer Resins

2.8.3.1 PVC/Vinyl Acetate Copolymers This is the most commonly used type of copolymer resin in plastisol applications. The main reason why PVC/vinyl acetate copolymers are incorporated into plastisol formulations is to reduce compound gelation and fusion temperature. The higher the level of copolymer resin in the plastisol formulation, the faster the compound gels and fuses. The same trend holds true for vinyl acetate content. The higher the vinyl acetate content in the copolymer resin, the faster the gelation and fusion rate. Typical applications where PVC/vinyl acetate copolymers are used include mechanical and chemically blown products, carpet backings, adhesives, and low-fusion dip coatings.

2.8.3.2 PVC/Carboxylic Acid Copolymers These copolymers are not as common as PVC/vinyl acetate copolymers, but do find use in plastisols. Like the PVC/vinyl acetate copolymers, they do speed fusion in plastisol formulations. However, their main use is to improve the adhesion of PVC plastisols to non-PVC substrates. Some of the substrates to which PVC/carboxylic acid copolymers improve adhesion are fiberglass, aluminum, galvanized metal sheet, and steel.[27] These materials normally contain hydroxyl groups on their surface. The carboxyl functionality of these resins has an affinity for these hydroxyl groups, thus improving the adhesion to these types of surfaces. Aminosilanes are also sometimes used to improve the adhesion between these types of surfaces with PVC, but they can also cause discoloration during the fusing of the finished article due to their tendency to react with labile chlorines on the PVC backbone and liberate hydrogen chloride.[34]

2.8.3.3 PVC/Vinyl Acrylate Copolymers These resins can be used in many of the plastisol applications where PVC/vinyl acetate copolymer resins are presently used. Although PVC/vinyl acrylate copolymer resins are more expensive than their PVC/vinyl acetate copolymer counterparts, they do offer two advantages. One benefit is that the viscosity stability of PVC plastisols containing PVC/vinyl acrylate copolymers is better over time than those based on PVC/vinyl acetate copolymers.

The other benefit is that PVC/vinyl acrylate copolymers tend to have lower volatile organic contents (VOCs) than PVC/vinyl acetate copolymers. This is because the reaction kinetics favor consumption of the vinyl acrylate monomer during polymerization, yielding very low levels of residual vinyl acrylate monomer. Most PVC/vinyl acetate copolymers have residual vinyl acetate monomer, which can volatilize during processing or during the use life of the article.[35] The lower VOC content typical of PVC/vinyl acrylate copolymer resins versus their PVC/vinyl acetate counterparts make them an option in automotive applications with stringent fog requirements.

2.9 RESIN SELECTION FOR PVC PLASTISOL APPLICATIONS

2.9.1 Resin Selection Manufacturing Issues Common to Most PVC Plastisol Applications

2.9.1.1 Moisture Pickup Excessive moisture pickup generally results in issues with product porosity and surface defects. The standard approach to reducing the amount of free water present is to add calcium oxide, which reacts with the water and forms calcium hydroxide. Since the surfactants used to coat the resin particles are notoriously hydrophilic, another way to reduce water pickup is to use dispersion resins containing lower surfactant levels or resins coated with less hydrophilic surfactants. Molecular sieves designed to absorb water can also be used to combat moisture pickup, but generally are less cost-effective than calcium oxide.

2.9.1.2 Air Entrapment Air entrapment causes the same types of issues as moisture pickup in the final product. Many of the surfactants used in dispersion resins hinder air release. This can be overcome by changing or reducing the amount of surfactant in the plastisol formulation through resin selection. Of course, reducing the viscosity of the plastisol aids in air release as well as the use of additives that assist "bubble break."

2.9.1.3 Mold Release After the part is molded, it needs to be removed from the mold. Although the residual surfactants coating the dispersion resins increase water pickup, they tend to make excellent mold release agents. If moisture pickup and/or air entrapment are issues, there are other additives available to improve mold release that permit the use of resins with lower surfactant levels.

2.9.1.4 Plateout Plateout can become an issue in plastisol molding operations as well as other plastisol applications where embossing rolls or other metal surfaces come in contact with the product surface. As plastisol molds are used repeatedly, material deposits can begin to form on the mold. These deposits can then cause defects in the final molded article. Plateout deposits that form on embossing rolls or other metal surfaces can also create surface defects in the final product.

Although dispersion resin surfactants aid in mold and metal release, they have been implicated in many plateout issues, and are one of the first things formulators consider when trying to reduce or eliminate these problems. The calcium oxide used to combat moisture pickup issues in plastisols has also been linked to plateout issues in some applications.

2.9.2 Resin Selection for Specific PVC Plastisol Applications

Unlike other large-volume flexible PVC applications such as wire and cable, the manufacturing processes used to make PVC plastisol-based products are quite varied. Obviously, resin selection for PVC plastisols is governed as much by the manufacturing process as by the end use application. The viscosity characteristics imparted to the plastisol by the resin are a key factor in resin selection. The use of copolymer resins in plastisol manufacturing processes will be discussed in Section 2.9.3.

Some of the larger-volume plastisol processes are described below:

2.9.2.1 Resilient Vinyl Flooring Resilient vinyl flooring is the largest consumer of PVC dispersion resins. A typical resilient flooring product construction is shown in Fig. 2.4. This figure details three of the distinct components commonly found in resilient vinyl flooring constructions: the substrate, the gel/foam layer, and the wear layer. We will discuss PVC resin selection for the gel/foam layer and the wear layer.

2.9.2.1.1 Gel/Foam Layer Most resilient flooring manufacturing processes coat an azodicarbonamide-containing or mechanically foamed plastisol formulation onto a substrate. It is desirable to achieve a product with consistent foam density throughout, with small, uniform cells. This yields a more durable product with better resistance to deformation over time. As stated many times before, the key to achieving a

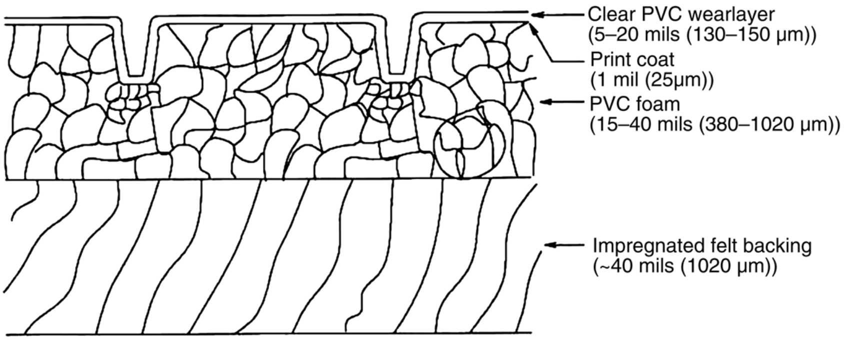

Figure 2.4 Cross-section of continuous flooring.

good cell structure is by achieving a thoroughly fused product. Although lower-molecular-weight resins are commonly used for foam applications, the improved mechanical properties of the higher-molecular-weight resins tend to make them the preferred choice in this application. Homopolymer dispersion resins with *K*-values ranging from 65 to 73 are commonly used in resilient flooring applications.

Certain resins contain surfactants that hinder air release. Also, resins with higher residual surfactant levels also tend to yield better results in foam applications. This is due in part to the fact that air release properties normally get worse as resin surfactant levels increase. Although poor air release is normally considered a problem in plastisol applications, it is actually a benefit in foam applications. Since a plastisol with poor air release has more difficulty releasing the gas generated from the azodicarbonamide decomposition, more gas is retained within the compound matrix, thus yielding a lower product density. Copolymer resins often find use in the gel/foam layer due to their ability to produce superior foams through their improved gelling and fusion characteristics.

In most resilient flooring applications, the product is gelled on the substrate without decomposing the azodicarbonamide. After this, it will go through a printing process. Some of the inks used in the printing process will contain additives such as trimellitic anhydride or benztriazole that inhibit the "kicker" or additive that catalyzes the decompsition of the azodicarbonamide. By applying the azodicarbonamide inhibitors in specific patterns onto the sheet, embossed patterns can be created without the use of downstream embossing rolls.[36] After the printing process, the gelled product will go through an oven to decompose the azo blowing agent and yield the final foamed sheet product. A potential benefit to using lower-molecular-weight homopolymer resins or copolymer resins is improved adhesion between the substrate and the gel/foam layer. Of course, the ability of a plastisol to wet and penetrate the substrate is governed in part by resin surfactant type and level.

Although azo foams predominate, mechanical foams are an option for resilient vinyl flooring. The resin selection guidelines for mechanical foam products are similar to those for azo-based products.

2.9.2.1.2 Wear Layer Clear PVC plastisols are typically used to coat the gel/foam layer to provide a wear layer for resilient flooring products. Durability and clarity are the two characteristics considered most important for this application. Unfortunately, many of the resin characteristics that are a benefit to one of the above characteristics are often detriments to the other. Durability characteristics such as abrasion resistance are maximized through the use of high-molecular-weight resins. Unfortunately, lower-molecular-weight products often provide superior clarity due to improved fusion characteristics.

The wear layer formulations tend to contain low levels (25–40 phr) of plasticizer in order to maximize abrasion resistance and durability. However, the flow characteristics of these formulations tend to be poor due to the low levels of plasticizer. One way to attack this issue is to use viscosity-reducing plasticizers such as 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB), which partially volatilize during fusion and create a case hardening effect at the wear layer surface. Another way to attack this problem is to use resins with higher residual soap content to reduce plastisol viscosity. Unfortunately, this approach can create issues with clarity and air release. Yet another way to counter the viscosity issue is to use blending resins. The drawback to this is that mixtures of blending resins and dispersion resins of equivalent K-value tend to be slower-fusing and often have poorer physical properties than plastisols based on straight dispersion resin.

Many factors entering into the resin selection equation for wear layers have been described above. The industry tends to use the following approach in wear layer products. In order to enhance durability, fairly high-molecular-weight resins with K-values ranging from 70 to 84 are typically used with low levels of plasticizer. Clarity is enhanced by reducing the residual surfactant level on the resin and by selecting surfactants with refractive indices close to that of PVC. Blending resins, viscosity-depressing additives, and viscosity-depressing plasticizers are normally used to lower the viscosity of these lightly plasticized formulations.

Most PVC wear layer topcoats now have a thin coating of crosslinked polyurethane over the PVC wear layer to enhance durability.

2.9.2.2 Knife and Roll Coating Applications The rheological behavior required for plastisols in knife and roll coating applications are similar. However, the type of substrate being coated plays a large role in plastisol rheological property requirements, and therefore plays a key role in resin selection. Plastisols with high yields and/or high viscosities at low shear rates are preferred for loosely woven substrates. Plastisols with low yields and/or viscosities at low shear rates tend to work better for tightly woven or continuous substrates. Products with lower viscosities under high-shear conditions are also preferred in knife and roll coating applications, since these characteristics tend to facilitate higher line speeds.[37] The molecular weight of the resin used is dependent on the manufacturer's ability to fuse the product in his process as well as the product's end use application.

Substrate adhesion, or lack thereof, is also an important factor in many spread and roll coating applications. The surfactant level and type in the dispersion resin play a large role in this, with lower surfactant levels generally yielding improved substrate adhesion. Also, the resin molecular weight can factor into the equation. The use of lower-molecular-weight resins will normally improve adhesion to a substrate versus higher-molecular-weight resins under equivalent process fusion conditions. However, in order to achieve good adhesion, the plastisol must be able to have a sufficiently low surface tension and good compatibility with the substrate in order to wet it and form a continuous bond.

For azo-based plastisol foam applications, a resin system that begins gelation at temperatures below the initial onset of azo blowing agent decomposition is desirable. Faster gelling systems can also help minimize the amount of entrapped air that escapes from a mechanically foamed product. Higher resin surfactant levels tend to reduce the ability of a plastisol to release air or gas prior to gelation and can help to lower the blown product density of both mechanical and azo foam plastisol formulations. There are special dispersion resins available with surfactant coatings that improve plastisol foaming characteristics.

2.9.2.3 Plastisol Molding Processes The use of copolymer resins in plastisol molding processes will be discussed in Section 2.9.3.

2.9.2.3.1 Dip Coating This is a very common molding technique and one of the simplest. A male mold is dipped into a plastisol tank and removed. Then the mold is normally sent through an oven to complete the fusion process. There are two common techniques: the "cold dip" and the "hot dip."

The "cold dip" process uses a non-preheated male mold. Because of this, the plastisol is not partially gelled onto the mold when the mold is removed from the plastisol. Resin systems that promote medium to high viscosity at low shear, high yield, and a fast gelation rate tend to be preferred in this process. Thus, the formulator should choose resin systems that are susceptible to viscosity effects induced by thixotropes.[38]

The "hot dip" process uses a preheated male mold. Since the plastisol has the opportunity to gel around the mold prior to removal from the plastisol, it is easier to achieve a more uniform coating thickness. Resin selection choices that affect the gelation of the plastisol are highly process-dependent. However, blends of GP dispersion grade resin with a K-value ranging from 64 to 74 with suspension grade blending resin are common in "hot dip" molding processes.[39] Resin systems that promote medium to high viscosity at low shear rates are preferred. The high yield and fast gelation plastisol characteristics desirable in cold dip molding processes are not as critical for hot dip molding processes. Another benefit of the "hot dip" process is that greater surface detail can be achieved with this method than with the "cold dip" process.

2.9.2.3.2 Slush Molding The typical example of a slush molded product is the typical rubber boot or overshoe. Plastisol is normally introduced into a preheated female mold. The plastisol then begins to gel along the interior surface of the mold. After sufficient gelation occurs, the remaining ungelled plastisol is dumped out of the mold and reused. The mold containing the gelled plastisol is then subsequently heated until the plastisol fuses completely. The finished article is then removed from the mold.

Low to medium viscosity at low shear rates and the absence of thixotropy are normally desirable characteristics for slush molded plastisol formulations. These formulation traits will facilitate drainage after the gelation step and leave a part with a minimum of drip and run marks on the interior skin surface.[40] Resin selection can help yield plastisols with these desired rheological characteristics.

There are several features of this process that are affected by resin selection. Besides fusion and gelation, mold release is also impacted by resin selection. Resin selection factors involving the mold release properties imparted by surfactants have already been detailed. The process of removing the part from the mold can sometimes tax the physical properties of the final product. Fully fused higher-molecular-weight resins have more resistance to the physical deformations that occur during this process. They also offer less tack and therefore improved mold release characteristics at any given temperature and equivalent surfactant level versus their lower-molecular-weight counterparts.

Another potential issue in the slush molding process is shrinkage of the part upon cooling. Although the shrinkage is only a few percent at most, defects can occur in certain areas depending on the part design. Completely fusing the part in the mold will help in most instances. Depending on the manufacturing process, a higher-molecular-weight resin system with improved physical properties or a faster-fusing resin system can also reduce defects of this type.

2.9.2.3.3 Rotational Molding The classic example of this molding technique is the inflatable PVC ball. PVC plastisol is poured into the mold. The mold is then placed into a curing oven and rotated along at least two axes until the plastisol cures. After the plastisol cures, the mold is cooled and the article is removed.

Low to medium viscosity at low shear rates and low thixotrophy are generally beneficial for rotational molding compounds. Also, the plastisol must readily wet the mold surface as the mold is rotated. Resin selection can aid the formulator in both of these areas.[40]

2.9.2.3.4 Hot Melt Molding The classic example of this type of article is the PVC fishing lure worm. The PVC plastisol is heated to a molten state and undergoes fusion. After the liquid is heated and fused, it is poured into a mold and cooled. When the finished article has cooled, it is removed from the mold. This type of molding requires highly plasticized formulations in order to have a material with sufficiently low melt viscosity to facilitate pouring. Since this material is often kept in a molten state for long periods of time prior to molding, these formulations have to be well stabilized.

Lower-molecular-weight dispersion resins with K-values ranging from 57 to 62 are preferred for several reasons. The main reason is that lower-molecular-weight resins have better flow properties at any given temperature than higher-molecular-weight resins. The improved flow properties help simplify molding, and the lower viscosity also yields better air release properties in the molten state. Copolymer resins are also useful in reducing melt viscosity.

The second benefit to using lower-molecular-weight resins is that if one can process the melt at a lower temperature, the stabilizer demand is less and the processor should encounter less discoloration over time when the material is maintained in a molten state during the molding process. Although higher-molecular-weight resins are more difficult to process in this manner, they experience less plasticizer exudation over time at the high plasticizer loadings necessary to mold products with this process.

2.9.2.4 Dispersion Resins for Clear Applications One of the problems with the surfactant coatings normally found on dispersion resins is that they create issues with clarity. There are dispersion resins available that use low levels of carefully chosen surfactants to yield clearer products than those made from typical dispersion resins. Although careful surfactant choice can help minimize the issues associated with reduced surfactant levels on dispersion resins, plastisols based on these resins are more likely to require other formulation additives to achieve desired rheological properties than typical plastisol resins.

2.9.2.5 Dispersion Resins for Low-Fog Automotive Applications My minivan's dashboard has an olefin skin; however, I still have to clean fog off of my windshield from time to time. Even though PVC has been wrongly implicated in many automotive fogging issues, PVC-based products used in above-the-beltline applications must still meet fairly stringent fog requirements. Most of the residual surfactants coating typical dispersion resin particles are too volatile for many automotive applications requiring low fog.

Because of the volatility issues with dispersion resin surfactants, some manufacturers have used lower-molecular-weight nondispersion suspension resin with K-values ranging from 60 to 64 in slush molded products for automotive applications. However, resin manufacturers have developed special dispersion resin grades for applications requiring reduced volatility. These grades normally use higher-molecular-weight surfactants in order to achieve low levels of fog.

2.9.3 Applications for PVC Copolymer Resins in Plastisols

The most common PVC copolymer resin type used in plastisol formulation is the PVC/vinyl acetate copolymer, and we will concentrate on the use of this type of copolymer resin. PVC/vinyl acetate copolymers are normally used to speed gelation and fusion in plastisol compounds. This provides benefits in many different plastisol applications. The downside to the improved gelation and fusion characteristics is that plastisol compositions containing PVC/vinyl acetate copolymers have worse shelf stability and poorer physical properties than the same compositions based solely on homopolymer resins of the same molecular weight. Another negative characteristic of these resins is that they tend to be less heat-stable than their homopolymer counterparts.

2.9.3.1 Mechanically Foamed Products Mechanically foamed products use high-speed impellers to entrap large quantities of air in the plastisol. Unfortunately, the air entrapped in the plastisol escapes quickly over time. When this occurs, the cell structure begins to collapse, yielding an inconsistent cell structure with non-uniform foam density throughout the finished product. By incorporating a PVC/vinyl acetate copolymer resin into the plastisol formulation, one can lower the gelation and fusion temperatures of the plastisol. By doing this, one can minimize both air release and the number of collapsed cells in the foam during the gelation and fusion process, thus yielding a more uniform final product with lower density.

2.9.3.2 Chemically Blown Products PVC/vinyl acetate copolymers have similar benefits in chemically blown plastisols; however, the mechanisms are slightly different. In chemically blown products, the blowing agent decomposes during the curing of the plastisol. In order to insure optimum cell structure, the plastisol must be somewhat fused when the blowing agent decomposes.

If the plastisol is not sufficiently fused when the blowing agent is decomposing, large amounts of gas can escape from the plastisol, increasing the density of the final product. If the degree of plastisol fusion is poor, cells will begin to form, but these cells will tend to collapse, since the cell walls of poorly fused plastisols have difficulty stretching to accommodate the expansion of the gas. This yields a poor cell structure with inconsistent foam density.

A well-fused plastisol resolves both of these issues. Much less gas will escape from the foam, and the cell walls have enough elasticity to maintain their cell structure, yielding lower product density, good cell structure, and consistent physical properties in the final product. Care must also be taken to ensure that the plastisol is not too thoroughly fused when the azodicarbonamide gas decomposition begins. A fully fused product will resist cell expansion more so than one with less complete fusion. The fusion conditions necessary to obtain maximum cellular expansion are extremely formulation dependent and are best determined experimentally.

2.9.3.3 Carpet Backings Most carpet backings are foamed, so the benefits of PVC/vinyl acetate copolymers described above for foaming applications hold true. The other major consideration is the type of carpet fiber used in the product. Many of the olefin- and nylon-based carpet fibers will melt or deform at typical plastisol curing temperatures. By using PVC/vinyl acetate copolymer resins, one can more completely fuse the carpet backing at lower temperatures without deforming or damaging the carpet fibers.

2.9.3.4 Adhesives The benefits of fast-fusing adhesives are intuitively obvious. The faster an adhesive cures, the quicker two surfaces can be bonded, yielding higher throughput rates in a manufacturing process. Also, in many applications, heat is not applied directly to the adhesive itself, but to the exterior surface of one of the materials being bonded. Thus, heat must travel through material in order to cure the adhesive. The lower the temperature required for curing the adhesive, the more easily can two surfaces be bonded in this manner.

Adhesives are an area where PVC/carboxylic acid copolymer resins sometime find use. As stated before, these resins have an affinity to polar, hydroxyl-laden surfaces and often yield improved adhesion to these types of surfaces.

2.9.3.5 Dip Coatings There are sometimes benefits to using PVC/vinyl acetate copolymers in both "hot dip" and "cold dip" processes. In "hot dip" applications, a faster-fusing material will allow for a thicker layer of gelled plastisol to form on the side of a mold when the hot mold is immersed in the plastisol. In both "hot dip" and "cold dip" applications, quicker gelation and fusion can result in a more uniform product thickness and fewer surface defects due to drips and other plastisol flow issues prior to gelation.

2.9.3.6 Hot Melts Using PVC/vinyl acetate copolymers will permit the processing of hot melts at lower temperatures due to viscosity reduction of the melt itself. If the hot melt can be processed at lower temperatures, color shifts due to long dwell times in the molten state can be reduced in some cases. Residence time of the molten plastisol in the heated tank should be carefully monitored.

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APPENDICES

Appendix 2.1 PVC Resin Molecular Weight Conversion Table

Inherent Viscosity, D-1243	Relative Viscosity, D-1243	*K*-Value, DIN 53726	Degree of Polymerization
0.52	1.60	50	420
0.68	1.82	57	625
0.73	1.89	59	690
0.79	1.96	61	800
0.82	2.03	62	850
0.91	2.17	66	925
0.93	2.20	67	1005
0.95	2.27	68	1045
0.98	2.30	69	1130
1.01	2.36	70	1250
1.05	2.42	71	1295
1.08	2.48	72	1340
1.10	2.51	73	1400
1.25	2.80	78	1780
1.34	2.97	80	2100
1.44	3.20	83	2400

Source: Formosa Plastics Corporation, USA technical literature.

Appendix 2.2 Summary of US Manufactured Suspension and Mass PVC Resins

Formosa Homopolymer Suspension PVC Resins

Product Name	Inherent Viscosity	Relative Viscosity	*K*-Value	Applications[a]
Formolon 608	0.68	1.82	57	1
Formolon 614	0.73	1.90	58	1,2,3,4
Formolon 616K	0.79	2.00	60	1,2,3,4
Formolon 622	0.91	2.17	65	4
Formolon 622F	0.91	2.17	65	4,5,8
Formolon 622S	0.91	2.17	65	2,3,4
Formolon 676	0.96	2.26	67.5	2,4,5,6,8,9
Formolon 680	1.01	2.34	69	5,8,9
Formolon 690	1.10	2.51	73	5,8,9

Georgia Gulf Homopolymer Suspension PVC Resins

Product Name[a]	Intrinsic Viscosity	Relative Viscosity	*K*-Value	Applications[a]
PVC 1060/2060	0.60	1.70	53	1
PVC 1066/2066	0.68	1.84	56	1
PVC 1070/2070	0.70	1.87	57	1
PVC 1079/2079	0.79	1.95	61	2,3,4
PVC 1082/2082	0.82	2.03	62	5,6,7
PVC 1091	0.90	2.13	65	4
PVC 1092/2092	0.92	2.20	66	5,8
PVC 1095/2095	0.95	2.25	68	5,8,9
PVC 1100/2100	1.01	2.39	70	5,8,9
PVC 1110	1.09	2.50	74	5,8,9
PVC 5305	0.73	1.93	59	2,3,4
PVC 5385	0.90	2.19	65	4
PVC 5395	0.95	2.28	68	5,8,9
PVC 5415	1.02	2.40	70	5,8,9

OxyVinyls PVC Homopolymer Suspension and Mass Resins

Product Name[c]	Relative Viscosity	Intrinsic Viscosity	*K*-Value	Applications[a]
OxyVinyls 185	1.82	0.68	56	1,3,4
OxyVinyls 185F	1.82	0.68	56	1,3,4
OxyVinyls 190F	1.90	0.73	58	2,4
OxyVinyls 195F	1.96	0.78	60	2,4
OxyVinyls 200F	2.04	0.83	65	5,7,8
OxyVinyls 216	2.16	0.90	65	4
OxyVinyls 220F	2.18	0.92	65	5,8
OxyVinyls 222	2.19	0.92	65	4
OxyVinyls 222S	2.19	0.92	65	5
OxyVinyls 225	2.17	0.91	65	5
OxyVinyls 225M	2.17	0.91	65	5
OxyVinyls 225P	2.19	0.92	65	5
OxyVinyls 226F	2.24	0.95	67	5,7,8,9
OxyVinyls 240	2.37	1.02	70	5,7,8,9
OxyVinyls 240F	2.37	1.02	70	5,7,8,9
OxyVinyls 255	2.55	1.12	73	8,9
OxyVinyls 255F	2.55	1.12	73	5,7,8
OxyVinyls 280	2.80	1.25	78	5
OxyVinyls 310	3.12	1.41	83	5,9
OxyVinyls 355	3.55	1.60	88	5
OxyVinyls 450F	2.24	0.95	67	5,7,8
OxyVinyls 500F	2.45	1.07	71	5,8

Shintech Suspension PVC Resins

Product Name	Intrinsic Viscosity	*K*-Value	Applications[a]
SE 650	0.68	57	1
SE 750	0.74	59	1,2
SE 800	0.80	61	2,3,4
SE 950	0.90	66	4
SE 1100	0.95	68	4,5,6,7,8
SE 1150	0.97	68	5
SE 1200	0.99	69	8,9
SE 1300	1.04	71	8,9
SE 1400	1.10	73	8

[a] *Legend*: 1, rigid molding; 2, rigid film/sheet; 3, rigid foam; 4, rigid extrusion; 5, flexible film/sheet; 6, flexible foam; 7, flexible molding; 8, flexible extrusion; 9, wire and cable.

[b] Note that Georgia Gulf 2000 series resins have lower gel and contamination levels than 100 series resins.

[c] In OxyVinyls resins, F = film grade, M = mass resin, P = pipe grade, and S = siding grade.

Appendix 2.3 Summary of US Manufactured Specialty PVC Resins

Formosa Homopolymer Specialty Resins

Product Name	Intrinsic Viscosity	Relative Viscosity	*K*-Value	Applications[a]
Formolon 10	0.98	2.30	68	1,2,3,5,12,13,15
Formolon 24	0.90	2.15	65	1,3,7,9,13
Formolon 24A	0.90	2.15	65	1,3,7,9,13
Formolon 28	1.20	2.65	75	2,3,6
Formolon 34	0.90	2.15	65	3,7,9,13
Formolon 38	1.20	2.65	75	2,3,6
Formolon KVH	1.20	2.65	75	2,3,6
Formolon NV	1.30	2.90	80	3,7,9
Formolon 411	1.13	2.57	74	2,3,12,13
Formolon 440	1.13	2.57	74	2,3,12,13
Formolon 442	1.04	2.40	70	3,5,6,7,8
Formolon 443	0.96	2.25	67	2,3,10
Formolon 1069	1.27	2.83	79	3,5,10
Formolon 1071	1.27	2.83	79	3,5,10
Formolon 1075	1.13	2.57	74	2,3,5,10
Formolon 230	1.07	2.45	71	Blending resin
Formolon 260	0.87	2.10	63	Blending resin
Formolon 260C	0.87	2.10	63	Blending resin
Formolon 360	0.87	2.10	63	Blending resin

Formosa Copolymer Specialty Resins

Product Name	Intrinsic Viscosity	Relative Viscosity	*K*-Value	Applications[a]
Formolon 40	1.04	2.40	70	7,8,13,16
Formolon 45	1.10	2.50	73	7,8,13,16
Formolon 265	0.77	1.95	59	Blending resin

Formosa Suspension Copolymer Resins

Product Name	Intrinsic Viscosity	*K*-Value	BVA %	Applications[a]
Formolon 113	0.48	48	13	VCT, sol. coatings
Formolon 165	0.56	51	13	VCT, sol. coatings
Formolon 168	0.63	54	10	VCT, sol. coatings, cal. film
Formolon 171	0.69	56	10	VCT, sol. coatings, cal. sheet
Formolon 172	0.69	56	10	Sol. coatings, ext./cal. film
Formolon 186	0.69	56	14	Sol. coatings, ext./cal. film

PolyOne Specialty Resins

Product Name	Intrinsic Viscosity	Relative Viscosity	*K*-Value	Applications[a]	Miscellaneous Information
Geon 120X400	1.01	2.38	70	1,2,9,11	Low emulsifier levels
Geon 121A	1.17	2.66	76	3,4,5,6	
Geon 121AR	1.20	2.71	77	1,5,6	Excellent air release
Geon 124A	0.85	2.11	64	1,3,5,6	Fast-fusing
Geon 129	1.25		82	12	Low fog
Geon 136	1.03	2.42	70	7,8,13	4% vinyl ester copolymer
Geon 137	1.11	2.56	73		Carboxyl functional copolymer
Geon 138	1.20	2.71	77	7,8,13	4% vinyl ester copolymer
Geon 140X466	0.66	1.75	56	14	
Geon 140X484	0.84	2.13	63	14	
Geon 140X497	0.97	2.32	68	14	

(*Continued*)

PolyOne Speciality Resins *Continued*

Product Name	Intrinsic Viscosity	Relative Viscosity	*K*-Value	Applications[a]	Miscellaneous Information
Geon 173	1.00	2.37	69	10,15	Good clarity
Geon 178	1.21	2.72	77	10,15	Good clarity
Geon 179	1.20	2.71	77	10,15	Good clarity
Geon 180X5	0.90	2.20	66	3,8,13	Foam applications
Geon 180X7	0.90	2.20	66	3,8,13	Foam applications
Geon 186A	0.98	2.34	69	3,8,13	Foam applications
Geon 213	0.85	2.11	64		Blending resin
Geon 217	0.92	2.23	67		Blending resin
Geon 218	0.74	1.93	59		Blending resin
Geon 471	1.02	2.40	70		High porosity
Geon 3400	1.34[b]				Low gloss

[a] *Legend*: 1, GP plastisols; 2, strand coating; 3, spread/roll coating; 4, spray coating; 5, dip coating/molding; 6, slush/rotational molding; 7, medium- to high-density foams; 8, low- to medium-density foams; 9, resilient flooring foam layer; 10, resilient flooring topcoat; 11, artificial leather; 12, automotive; 13, inks; 14, powder coating; 15, thin films; 16, adhesives.

[b] Resin is partially crosslinked, and viscosity cannot be determined by traditional methods. This value of the intrinsic viscosity is an estimate based on how the resin behaves in PVC formulations.

CHAPTER 3

PVC Special Products

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3.1 PVC LATEX

PVC latex is a colloidal dispersion of a vinyl chloride polymer or copolymer in water, usually of 0.25 μm or smaller spherical particles. Currently available products are typically copolymers and terpolymers. The applications for PVC latex include:

[1] Section 3.1.
[2] Section 3.2.
[3] Section 3.3.

Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

- Coatings and saturants for fabric, paper and leather
- Pigment and ink binders
- Primer, tie-coat, and barrier coatings
- Pressure-sensitive and heat-sealable adhesives
- Binders for flame-retardant coatings
- Release coatings for tapes, strippable coatings

PVC latex coatings are known for abrasion resistance, toughness, flame retardance, and resistance to water, oils, and chemicals. They are applied by most of the common coating methods, including air knife, knife, roll, conventional and airless spray, brush, and curtain coating. Saturation, dipping, and slush coating are also used. Although PVC latex applications comprise less than 1 percent of the PVC market, they are technically significant and stimulating.

3.1.1 Types of PVC Latex

PVC/VA copolymers have perhaps the longest history of use. The major North American supplier is the Noveon division of Lubrizol, supplying products under the trade name Vycar® with designations corresponding to the Geon® grades once supplied by BFGoodrich. The grades now supplied include Vycar® 351 and 352, both at 57 percent solids with pH of 10.3 and glass temperatures (T_g) of 62 and 69 °C, respectively (thus neither is film-forming at room temperature). These grades are usually further compounded and are often found in paper saturants, sometimes blended with acrylic latex. Vycar® 460 × 104 is a carboxylated grade (i.e., a terpolymer), providing increased stiffness and adhesion. Vycar® 460 × 95 is carboxylated and heat-reactive, pointed at lamination and heat-sealing applications. Further data is available at the Noveon website.

PVC/VA latex is also available from Solvay (Solvin® 072GA) and BASF (Lutofan® DS2380). These grades are aimed at adhesive, ink, and lacquer markets. The number of suppliers and available grades of PVC/VA latex have decreased notably. One factor has been integration forward into supply of paint, ink, and coatings, instead of ingredients for their manufacture.

Preplasticized PVC/VA grades are also available. Phthalate-plasticized grades include Vycar® 580 × 182, 580 × 180, 578, and 580 × 83, with T_g of -14, -12, $+11$, and $+17$ °C, respectively. This is a great convenience for the formulator. Flame-retardant phosphate-plasticized grades include Vycar® 577 and 575 × 43. T_g of these grades are 19 and 29 °C, respectively. Vycar® 590 × 4 with a T_g of 20 °C, is, in addition, carboxylated and heat-reactive. Vycar® 552 is a 70/30 PVC-nitrile rubber latex blend for oil resistant, plasticizer-free applications, with a T_g of 4 °C.

A PVC/VA/ethylene terpolymer, Airflex® 430 emulsion, is available from Air Products, with a T_g of 0 °C. It is aimed at moisture barrier coatings, caulks, and sealants. Air Products also supplies PVC/ethylene emulsions: Airflex® 4500, 4514, and 4530, with T_g of 0, 14 and 30 °C, respectively (thus the first two are film-formers at room temperature). These heat-sealable products are used in adhesives, paint, and coatings for paper and fabric.

PVC/acrylic latex emulsions are also supplied by Noveon under the trade name Vycar®. The grades in the Vycar® 460 series, ×46, ×49 and ×119, have T_g of 7, 40 and 37 °C, respectively. They are carboxylated (thus terpolymers) and heat-reactive. Applications include lamination, heat sealing, saturation, and coating by a variety of techniques. PVC/acrylic polymers are generally superior to PVC/VA analogs in resistance to weathering. Grades for carpet backing and related applications include Vycar® 460 × 63 and 460 × 58, with T_g of 22 and 40 °C, respectively; both are carboxylated and heat-reactive. Stiffer products are provided by the Vycar® TN series, TN-816 and TN-810 having T_g of 47 and 55 °C, respectively. These grades are used for impregnation and saturation of fabric, which is then shaped and heat-set. A phosphate-plasticized PVC/acrylic for coatings is supplied as Vycar® 590 × 20. PVC/acrylic emulsions are also supplied by DSM under the trade name Haloflex®.

Although most PVC latex is produced by emulsion polymerization, a group of PVC/acrylic products, emulsions of solution copolymers, is supplied by Dow under the trade name Ucar® Vinyl Acrylic Latex. Grades include Ucar® Latex 300, 301, 357, and 367, with T_g of 2, 2–3, 12, and 10 °C, respectively. These grades are used in paint, industrial and architectural coatings. Ucar® 162, with a T_g of 3 °C, is pointed at caulking compounds. Ucar® 7659, with a T_g of 12 °C, is used in strippable coatings.

3.1.2 PVC Latex Properties

Total solids is the measure of the weight of polymer (or plasticized polymer) to the total weight, expressed in percent. PVC latexes are typically in the range of 50–60 percent solids, with overall specific gravity (SpG) of 1.1–1.3. PVC/VA latex grades have Brookfield viscosities in the range of 20–50 cP, emulsion-polymerized PVC/acrylics in the range of 20–150 cP, and solution-polymerized PVC/acrylic emulsions and PVC/ethylene emulsions in the range of 50–500 cP. The pH of most PVC latexes is alkaline, 8–11; some grades have acid pH, generally those with reactive —COOH groups, referred to as "carboxylated." On standing, pH can drop due to hydrogen chloride formation; thus storage at elevated temperatures is undesirable. It should, in addition, be assumed that the freeze–thaw stability of PVC latex is poor. The surface tension of PVC latex is typically 30–45 dyn/cm. This is usually low enough to disperse ordinary compounding ingredients. The use of additional surfactants or dispersion aids, when needed, should be adjusted so as not to alter the original pH (most PVC latex contains anionic dispersants).

3.1.3 Compounding PVC Latex

Compounding ingredients are usually added as water solutions, emulsions, or dispersions. This is generally more successful than direct addition of the ingredient, which may cause spots of local latex coagulation. Solutions added are typically of water-soluble thickeners and film formers, such as cellulose derivatives, additional surfactants, defoaming agents, biocides, additives to adjust pH, and heat-reactive crosslinking agents (generally formaldehyde-based resins). Water solutions generally require gentle agitation for several minutes.

Liquids such as plasticizers and low-melting ingredients such as waxes are added as oil-in-water emulsions. A number of waxes and resins are available from suppliers in emulsion form. If compatible with the latex in question, processing is greatly simplified. This is also the case if a preplasticized latex grade can be used. If not, emulsions are prepared either by a one- or two-step process. In the latter, a crude emulsion of, for example, plasticizer, water, and surfactant is prepared with an electric or air-driven stirrer. The crude product will have a considerable range of particle size. This is corrected by passage through a colloid mill, shear homogenizer, or other high-shear device, yielding a fairly uniform particle size, typically 1–5 μm.

Alternatively, the emulsion can be made in a single step with a suitable high-shear mixer. Such equipment is available from Arde Barinco ("Eppenbach" type mixers), Chemineer, Inc. ("Gifford-Wood" type mixers), Morehouse Cowles (Cowles Dissolver), Jaygo, Hochmeyer, Escher Wyss, and others. In most cases, oil is added to water gradually under high-shear mixing to form an oil-in-water emulsion. Others prefer an upside-down procedure, where water is added gradually to the oil, with a build in viscosity leading to increased shear, followed by inversion of the water-in-oil to an oil-in-water emulsion, the viscosity decreasing as inversion is completed. Emulsions of ester plasticizers are commonly run at 60–65 percent. Such levels generate a useful level of viscosity. When emulsion viscosity is too high, air entrapment is facilitated; when too low, the chance of separation, because of the difference in SpG, is increased. As a general rule, the stability of a plasticized latex decreases with the resin-solvating power of the plasticizer. As the size of the emulsified particle decreases, stability (and viscosity) increases. High surfactant concentration favors development of small particles. Generally, the viscosity of compounded latex increases for a day or two, then levels off (by or at which time it should be consumed in processing).

In a typical "upside down" emulsion preparation, a high-shear mixer is loaded with part A, comprising the plasticizer and surfactant. The latter may be a nonionic, but more usually oleic or other noncrystalline fatty acid (stearic acid tends to favor phase separation). Under high shear, part B is added gradually. It consists of water containing a nonionic surfactant, but more often a water-soluble organic base (metallic hydroxides also favor phase separation). This is most commonly ammonium hydroxide, thus forming ammonium oleate at the water–oil interface, putting the surfactant exactly where it is needed (a technique used in the coating industry for many decades). In combination with oleic or a similar organic acid, surfactants formed from morpholine are generally more effective than ammonium salts (at the expense of cost and problems with odor and toxicity).

The common usage of terms is that "dispersion" in latex refers to stable suspensions of solid rather than liquid materials. Common dispersions are of fillers, pigments, and flame retardants. These are generally made in two steps: dispersion of the powder in water containing surfactant(s), and generally a soluble polymer for thickening, at relatively low shear, followed by refining. At one time, ball mills were favored for the latter step. This is now the case only when particle agglomerates are very persistent. Common practice now is to refine the crude dispersion using a three-roll paint or ink mill. A number of passes through roll nips of increasingly tight settings are carried out until particle size distribution reaches the desired standard, as indicated, for example, per ASTM D1210, using a Hegman gauge (Paul N. Gardner Co.).

PVC latex can be blended with polyvinyl acetate (PVAc), acrylonitrile butadiene rubber (NBR), and acrylic latex of comparable pH and surfactant systems. Since such blends are commercially available, this practice, at one time very popular with paint and coatings, has fallen off.

3.1.4 Formulating PVC Latex

Essentially all of the plasticizers used in dry compounding of PVC can be used in latex. General purpose use is mainly of di-2-ethylhexyl phthalate (DOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP); DOA in low-temperature grades; and phosphates to provide flame retardance and polymeric esters where the lowest volatility and migration is desired. Epoxidised soybean oil (ESO) is often added both to plasticized and preplasticized grades. When used, the final product should be consumed quickly to prevent epoxide hydrolysis. A useful choice of stabilizer is about 1 part per hundred of resin (phr) of a hydrolysis-resistant organotin compound such as dibutyltin oxide (DBTO). The combination of DBTO and oleic (or other organic) acid probably generates an organotin carboxylate within the polymer matrix. Organotin carboxylates and mercaptides such as Thermolite® 31H (Arkema Group) have been used directly, but again the final product must be used promptly to forestall stabilizer hydrolysis. This is also the case with mixed metal stabilizers. Relatively slow hydrolyzing organophosphites can be used, with zinc octoate activation. In order to avoid gel formation, mixed metal or zinc-based stabilizers should not be used with carboxylated products.

Dibasic lead phthalate is technically effective, but undesirable from a toxicological standpoint. Inorganic stabilizers, such as coated hydrotalcite or zeolite, can be dispersed with fillers and pigments. An example is Halstab® 1214, DBTO-coated zeolite. With heat-reactive blends containing formaldehyde-based crosslinking agents (formaldehyde–urea or –melamine low polymers), dicyandiamide has been used extensively at about 1 phr as a heat stabilizer.

To obtain a suitable coating viscosity, and to prevent settling of filler particles, thickeners are often used. These are often low-cost natural products based on cellulose or casein. These are readily metabolized by many bacteria and fungi; therefore, a biocide should be included. Biocides in powder form such as Captan® (R.T. Vanderbilt) or Zinc Omadine® (Akcros) can be dispersed with fillers and pigments. A useful starting point level is 1 percent by weight of the natural polymer to be protected. Alternatively, a biocide water dispersion, such as Nuocide® 404-D (40.4%, International Specialty Products), can be used.

After consideration of the cost of added biocide, it may be useful instead to use a synthetic thickener, usually polyvinyl alcohol or a salt of polyacrylic acid, generally ammonium polyacrylate. The same result can sometimes be reached by blending with an aqueous polyvinyl acetate–alcohol or "carboxylated" acrylic emulsions or solutions. A combination of thickening and adhesion promotion often results. This can be the case as well with blends of polyurethane emulsions. For release coatings, on the other hand, blends can be made with low-molecular-weight polytetrafluoroethylene (PTFE) (e.g., DuPont TraSys®) or silicone emulsions (e.g., Rhodia Rhodorsil®) or with these in combination. As always, pH and type of surfactant should be matched. If the final product requires an extended shelf life (e.g., paint), biocides are usually included. Tributyltin compounds, such as Fungitrol® 334 (45.6 percent tributyltin benzoate, ISP) are very effective in outdoor exposure applications, but are subject to increasing regulatory pressure.

Latex Brookfield (20 rpm) viscosity of 100–250 cP is generally desirable for coatings using spray techniques, wire-wound rods, and air knives. A range of 500–2500 cP is more useful for reverse roll or knife-over-roll coating. With porous substrates such as fabric or paper, the nature of the web being coated, the need for more or less penetration and coating weight, and the thixotropic nature of the latex typically determine the coating method.

Most commercial grades of PVC latex are supplied with anionic surfactants as emulsion stabilizers. These tend to provide good mechanical (shear) stability and high wetting ability with regard both to further ingredients and coating substrates, but are not very good regarding resistance to foaming. When nonionic surfactants are used to disperse compounding ingredients, mechanical stability may be decreased, but resistance to foaming and pH stability are increased. If the starting emulsion has a pH below 9, added surfactants should be limited to anionic and nonionic types. The combination amine-plus-acid surfactants are very convenient in terms of rapid incorporation of ingredients, have good shear stability, but are typically inferior in pH stability and resistance to foaming. They are likely, from the residual amine content, to negatively affect color hold on aging. (Although no data has been reported with regard to latex compounds, by analogy, discoloration resistance may be mediated by soluble perchlorate salts or use of perchlorate-containing hydrotalcite.)

With low-shear mixing equipment, foam formation can be avoided or minimized by adjusting the mixing action to avoid formation of a vortex. With high-shear equipment, antifoam agents are added just prior to mixing. These include fugitive alcohols such as 2-ethylhexanol and a range of nonionic surfactants. Traces of silicone defoamers can be used if substrate adhesion is not a problem.

Plasticized flame-retardant coatings are best achieved by emulsifying phosphate plasticizers or using grades already containing them. This is often boosted by the addition of 3–8 phr of antimony oxide. Low-smoke flame-retardant compounds use emulsified zinc borate or hydroxystannate in place of, or in addition to, antimony oxide. Formulating with fillers and flame retardants follows dry compounding of PVC. Intumescent coatings are often based on PVC/VA or PVC/acrylic latex. In these cases, salts such as ammonium phosphate, melamine phosphate, or ammonium sulfamate are dispersed or dissolved, often by about 30 percent in water, and usually added, for best stability, after dispersing the emulsified plasticizer. (If the latex has great stability to addition of salt solutions, the reverse order is feasible.) The action of these salts to form an expanded char during flame conditions that is thermally nonconductive is enhanced by the presence of polyols such as pentaerythritol. Common systems might comprise 3–10 phr of an intumescent salt plus 1–2 phr of a polyol.

3.1.5 Processing PVC Latex

Dipping is used for thin coatings on nonporous or slightly porous substrates. The object is immersed and withdrawn, and the excess compound allowed to drain off. Coating thickness depends on the porosity of the substrate, compound flow properties, solids and viscosity, and dwell time. Saturation or impregnation is a variation. Porous substrates such as paper or fabric are immersed in the latex and excess compound is removed by passing through squeeze rolls. In this case, low-viscosity products are used, often with specific wetting agents added. In the case of paper or nonwoven fabric, the latex can be mixed with the fibrous pulp and precipitated onto the fibers by adding a coagulant such as alum. Then paper or nonwoven fabric is formed from the polymer-treated fibers. This technique is referred to as "wet-end" or "beater" addition (using paper industry jargon).

Latex compounds are often applied by spray methods. The compound must have good mechanical stability to prevent coagulation in the supply line or gun nozzle. Addition of minor amounts of 10 percent sodium tetraborate solution or of ethylene glycol can reduce premature drying in the nozzle, improving spraying ability. Both conventional and airless spray systems are used.

Several methods are used to coat continuous substrates (referred to as "webs," again taken from paper coating). When a single roll is used to pick up latex from a pan or trough and deposit it on the web, the process is referred to as "kiss coating." Coating weights are controlled by compound solids and viscosity, web tension, and the speed with which the coating roll is driven (usually opposed to the direction of web travel). Although precision in coating can be improved by use of smoothing bars on the latex coating, and by various roll arrangements to reduce variation in tension, the method, although inexpensive, is unsophisticated and not widely applicable. The process can be modified to use knife-over-roll coating for high-viscosity compounds, or wire-wound rod metering of coating weight with low-viscosity latex.

More precise coating weights are obtained using reverse roll coaters. In this technique, one roll picks up the latex compound from the reservoir, and transfers it through an adjustable roll nip, providing metering, to the web. Three- and four-roll combinations are used. The process is the latex equivalent to calendering dry compound. Roll arrangements can be made to provide for lamination of porous webs during coating. Reverse roll coaters can accommodate a wide variation in compound viscosity and a range of products from release coatings to adhesives.

Another precise technique suitable for low coating weights is the use of an air knife coater. Latex is applied to the web by a transfer roll and coating weight adjusted by air blowing at an angle to the web. Coating weight depends on solids and viscosity, but is adjustable by variation in air pressure. Both reverse roll and air knife coating can be automated to a closed loop system by automatic measurement of coating weight after drying controlling coater settings. Coating weight is accurately measured by an X-ray gauge, such as supplied by NDC Infrared Engineering, which differentiates between coating and substrate, unlike beta-ray thickness gauges.

Thin coatings are commonly applied to rough surfaces with a curtain coater, in which a metered curtain of low-viscosity latex is forced through an adjustable slot onto the web, the line speed of which is also a factor in coating weight.

Drying of latex compounds is usually done in zones to ensure a continuous film. The first zone is typically at about 100 °C to prevent blister formation, the second is at a temperature above that needed for film forming, and the final zone is set at fusion temperature. Fusion is often carried out with an infrared unit. Embossing, if required, is done in line after fusion. Printing of PVC-based films from latex usually requires vinyl resin ink. PVC/acrylic films are more receptive and are printed with a variety of inks.

3.1.6 PVC Latex Applications

Coating fabric with PVC latex improves resistance to abrasion and tear, water and stains, while providing color and texture. Applications include products such as luggage, tarpaulins, upholstery, wall coverings, and shades. PVC latex is also used as a primer for second coats of plastisol, organosol, or solution coating. In addition to improving adhesion to hydrophilic substrates, the latex primer acts as a barrier to excessive penetration of the subsequent coating. A starting point recipe based on PVC/Va (e.g., Vycar® 352) would include 20 phr DOP and 15 phr each of DOA and ESO as plasticizers, 30 phr titanium dioxide, 15 phr calcium carbonate, and 1 phr sodium acrylate thickener. The plasticizers would be added as 65 percent water emulsions, the filler and pigment as 50 percent emulsions and the thickener as a 5 percent solution. DBTO stabilizer at a 1–2 phr level could be added in the filler emulsion, plus a low level of benzotriazole UV light absorber if needed. For outdoor applications or wall coverings, it would be better to overcoat with an acrylic emulsion or coating containing a hindered amine light stabilizer. For such uses, a biocide would usually be added. The combination of plasticizers provides a good balance of properties at reasonable cost.

If flame retardance were an objective, a phosphate preplasticized grade (e.g., Vycar® 577) would be a good choice, perhaps in combination with ATH as filler. For automotive interiors, the above blend of plasticizers would generate unacceptable fogging. In this application, low-fogging preplasticized grades (e.g., Vycar® 578 and the 580 series) should form the starting point. Low-fogging products should avoid oleic or related acids and instead use anionic or nonionic surfactants in emulsion of ingredients.

Fabric saturation with PVC latex is also common. The fabric may be woven from pretreated yarn or saturated in finishing, in both cases typically at a pickup of 3–10 percent by weight. The treatment provides improved resistance to wear and stain, plus adhesion for subsequent lamination or coating, and the ability for dielectric heat sealing.

PVC latex provides a useful low-cost binder for more or less fluffy (the jargon here is “high-loft”) nonwoven products used in quilting, furniture padding, bedding, and sleeping bags. Properties include improved flame retardance, ability to survive solvent dry cleaning, and good “loft” retention. Improved resistance to dry cleaning and washing can be provided by using a reactive grade (e.g., Vycar® 480 series) in combination with 3–5 phr of a melamine or urea–formaldehyde resin. Where use of formaldehyde-containing products is undesirable, recourse should be to a heat-reactive PVC/acrylic (e.g., Vycar® 460 series). In such applications, zoned drying is generally used, at about 100 °C in the first zone and at about 175–180 °C in the second, with no heat but strong venting in the last; residence time in each is about 1 minute, depending on overall water content. The initial zone may include passage over a vacuum plate to draw the latex into the nonwoven web.

Automotive interior door panels often use PVC latex as a binder for a high-loft fabric bonded to a backing board. This is then covered with vinyl-coated fabric, and the entire assembly placed in a dielectric sealing press, where it is both heat-sealed and embossed. PVC latex-coated paperboard stock also finds use in various packaging applications. When PVC latex is used to saturate, rather than coat, paperboard, the products are suitable for preparation of molded mats.

Clear coatings based on PVC latex are common on products such as wallpaper, shelf paper, and book covers. Fine-particle silica or diatomaceous earth can be used at low loadings to limit gloss. This effect can also be achieved by blending with PVDC latex such as Vycar® 650 × 27 and 660 × 14. These products can also be used for moisture vapor barrier coatings. A special grade, Permax® 803 PVDC/acrylic copolymer, is used as a barrier in automotive underbody coatings.

3.2 SOLUTION PVC RESINS

Solution vinyl resins are copolymers and terpolymers of vinyl chloride. Although only a minor fraction of the PVC market, they are important in a variety of coatings, inks, cements and cast films. Vinyl chloride is polymerized in a solvent such as acetone with peroxide initiation. The solvent acts as a chain transfer agent, resulting in relatively low-molecular-weight products with typical number average values of 5000–50,000. For coating applications, this is desirable from solubility and rheological characteristics. Because of the method, the resins are free of residual surfactants. To hold a fairly narrow molecular weight distribution, the reaction is not driven to completion; residual monomers are removed and recycled. The polymer is recovered by precipitation with a nonsolvent, such as water, washed, centrifuged and typically dried in a two-stage process: a fluidized bed dryer following a flash dryer.

Functionality is introduced in several ways. Hydroxyl functionality is achieved either by partial hydrolysis of acetate groups in a PVC/VA polymer or by including a minor fraction of a hydroxyl-containing acrylic monomer, such as hydroxyethyl acrylate. Carboxyl functionality results from inclusion of maleic or acrylic acid monomers; epoxide groups from inclusion of a glycidyl ester.

The solution process generates irregular amorphous particles having a broad range of particle size (average particle size is often about 200 μm). Particle size distribution can be controlled by precipitation conditions, which also affect bulk density and porosity. Typical porosity is in the range of 0.25 g/cm^3, and bulk density about 0.4 g/cm^3. These parameters facilitate solution applications.

3.2.1 Types of Solution PVC Resins

Solution vinyl resins developed by Union Carbide are now sold under the trade name Ucar® by Dow Chemical. The current grades are listed in Tables 3.1(*a*) and (*b*). They include three molecular weight grades of PVC/VA (VYNS-3, VYHH, and VYHD), three of PVC/VA/maleic acid (VMCH, VMCC, and VMCA), two partially hydrolyzed PVC/VA grades (VAGH and VAGD), and three hydroxyacrylate terpolymers (VAGF, VAGC, and VROH). Specialty grades include a 40 percent solution of an epoxy functional PVC/VA (VERR-40), a maleate–hydroxyacrylate combination, (Ucarmag® 527), and a sulfonate functional PVC/VA (Ucarmag® 569). Except for VERR-40 (40 percent in methyl ethyl ketone (MEK)/toluene), the resins are white powders of bulk density 24–34 lb/ft^3 (0.38–0.54 g/cm^3), maximum water content of 0.5 percent, melting points of 93–135 °C, and 98 percent and more through 20 mesh.

PVC/VA resins for solution applications are also produced by suspension polymerization to controlled, relatively low molecular weight and particle size. Although not equivalent in all respects to solution-polymerized resins, particularly from containing residual surfactants, they are often used in similar applications. A range of grades is supplied by Wacker Specialties under the trade name Vinnol®. In this case, the weight percent (wt%) vinyl acetate is given in the grade designation.

TABLE 3.1(*a*) Dow UCAR Solution Vinyl Resins

	VYNS-3	VYHH	VYHD	VMCH	VMCC	VMCA	VERR
Wt% vinyl chloride	90	86	86	86	83	81	82
Wt% vinyl acetate	10	14	14	13	16	17	9
Third monomer					Carboxyl		Epoxy
Acid no.				10	10	19	
Epoxy equivalent weight							1600
Inherent viscosity	0.74	0.50	0.40	0.50	0.38	0.32	
SpG	1.36	1.35	1.35	1.35	1.34	1.34	
T_g (°C)	79	72	72	74	72	70	67
Viscosity, 25 °C (cP) (20% in MEK)	1300	600	200	650	100	55	

TABLE 3.1(*b*) Dow UCAR Solution Vinyl Resins

						Ucarmag®	
	VAGH	VAGD	VAGF	VAGC	VROH	527	569
Wt% vinyl chloride	90	90	81	81	81	82	85
Wt% vinyl acetate	4	4	4	4	4	4	13
Third monomer	Hydroxyl					Hydroxyl/ Carboxyl	
Hydroxyl no.	76	76	59	63	66	59	
Inherent viscosity	0.53	0.44	0.56	0.44	0.30	0.56	0.33
SpG	1.39	1.39	1.37	1.36	1.37	1.37	1.35
T_g (°C)	79	77	70	65	65	72	72
Viscosity, 25 °C (cP) (20% in MEK)	1000	400	930	275	70	720	850

Grade H 11/59 denotes 11 percent vinyl acetate, with a *K*-value of 59 (similar to VYNS-3). Vinnol® H 14/36 and 14/42 are similar to VYHD and VYHH. Wacker also supplies 15 percent vinyl acetate grades E 15/45 and H 15/50. In addition, high-VA-grades are provided (H 40/43, H 40/50, H 40/55, and H 40/60). Maleate terpolymers with pendant carboxyl groups are designated E 15/45M and H 15/45M, similar to VAGH and VAGD. Hydroxylacrylate terpolymers are designated E 15/40A, E 15/48A, and E 22/48A, similar to VROH, VAGC, and VAGF. Somewhat more limited ranges of products are supplied by Asahi Denka (Solution Vinyl 1000 series), Kaneka (Kanevilac®) and Sanmar Ltd of India (Chemplast series). PVC/vinyl isobutyl ether copolymers for many of the same purposes are supplied by BASF under the trade name Laroflex®.

3.2.2 Solvents for Solution Vinyl Resins

Solution viscosity of the Ucar® resins is given in Tables 3.1(*a*) and (*b*) at typical coating levels. It increases with increasing molecular weight and decreases with vinyl acetate content. Third monomers have variable effects, often increasing viscosity through van der Waals interactions. The Vinnol® 10–15 percent vinyl acetate resins and functionalized terpolymers have relatively similar solution viscosities. In general, as the ketone or ester component of the solvent is increased, viscosity decreases; the opposite occurs with increase in hydrocarbon diluent. Higher concentrations than those of Tables 3.1(*a*) and (*b*) can be reached with inclusion of more active solvents such as tetrahydrofuran or cyclohexanone. Commercial coatings tend to use blends of fast-evaporating (MEK, ethyl acetate), medium-evaporating (methyl isobutyl ketone (MIBK), butyl acetate) and slow-evaporating solvents (amyl acetate, cyclohexanone). As the rate of evaporation decreases (through increasing molecular weight of the solvent), solution viscosity tends to increase.

Hydrocarbon diluents are not in themselves solvents, but can be used to lower overall cost and may aid in solvent recovery. Aromatic hydrocarbons are the most effective and can be used in many cases to make up 33–67 percent of the solvent blend. Aliphatic hydrocarbons are not generally useful above 10 percent. Ketone solvents tolerate higher levels of diluents than esters and provide better shelf stability. Technical considerations, however, must be balanced against cost and environmental regulations.

3.2.3 Formulating Solution PVC

Because of their relatively low molecular weight, solution PVC/VA resins are formulated with plasticizer levels of 0–25 phr. These are useful not only in improving flexibility but also in minimizing solvent retention in the coating. Most commonly, general purpose phthalate plasticizers (DOP, DINP) are used. For increased flexibility, linear phthalates are used, and for least volatility, DIDP, DTDP, and trimellitates. Phosphate plasticizers are used in flame-retardant applications, and polymeric polyesters where resistance to migration or extraction is required.

Solution PVC/VA resins tend to be zinc-sensitive. Liquid Ba/Zn and Ca/Zn stabilizers with low zinc levels can be used, as well as zinc-activated phosphite liquids. Mixed metal stabilizers are not used with carboxylated resins because of the likelihood of gel formation, and epoxidized oils should be limited to those with single functionality such as epoxytallate ester. With a last of reactive carboxylate groups, ESO is used, often at 2–5 phr. Typically organotin carboxylates and mercaptides are used, at about 1 phr. Clear coatings are not recommended for outdoor use. Where indoor exposure to light from fluorescent fixtures is anticipated, UV light absorbers are included. Benzotriazoles are used other than for carboxylated grades; benzophenones may be used generally. A better approach is to overcoat with an acrylic coating containing a hindered amine light stabilizer.

Colorants are most commonly soluble organic pigments such as phthalo blue and green, and perylene and imidazolone pigments, added as liquid color concentrates. Inorganic pigments can be used—again usually as liquid or paste color concentrates, but should be free of reactive metals (zinc and copper). Synthetic iron oxides of all shades are useful, and are often combined with organic pigments for a brighter and more durable effect. It is, of course, possible to disperse pigments directly into a resin solution using a ball mill, three-roll paint mill, or high-shear dispersing equipment, but the volume of usage is generally such that use of predispersions is favorable. This is particularly the case with fine-particle carbon black, the most common black colorant. Aluminum powder and flakes are used for metallic coatings; copper and bronze should be avoided, using combinations of aluminum and organic pigments to achieve the desired effect. Colorants with basic pH must be avoided in formulating carboxylated grades, particularly with polyvalent cations (lead, zinc, chromium, and strontium).

Filler usage parallels standard PVC formulating, except that the use of hydrous fillers (ATH, magnesium hydroxide, hydrous silica, zeolite) can lead to viscosity instability, particularly with carboxylated grades. The latter are sufficiently sensitive that silica or ATH surface treatments of titanium dioxide (a benefit everywhere else) can destabilize solution viscosity. In some cases, viscosity build can be reversed with low levels (0.25–1 percent) of citric acid or lauryl acid orthophosphate.

Solutions of PVC/VA polymers can be blended with most acrylic resins to provide useful coatings, but with few other polymers. Carboxylated and epoxy-functional grades can be combined to provide heat-crosslinkable blends, at the expense of limited shelf stability. Hydroxyl-modified grades have broader compatibility and may be blended with alkyd, urea, melamine, and epoxy resins, and with urethane prepolymers. Such blends can be heat-crosslinked, resulting in tough, chemical-resistant films. Urethane blends are characterized by high mar and scratch resistance.

Thixotropic agents used to increase coating viscosity for building thick films include treated clays and silica gel. These are also used to reduce surface gloss. Use of a slow-evaporating solvent such as cyclohexanone provides a leveling agent for such systems. Proprietary additives (e.g., Byk Chemie BYK-052) can improve solvent release. With judicious choice of solvent blend, solution PVC inks compete effectively with their far more hazardous fast-drying nitrocellulose-based predecessors.

Solution vinyl resins can be readily dissolved by slow addition to solvent at room or elevated temperature, either with a low-speed turbine mixer or with a high-speed mixer such as a Cowles® dissolver. Resin feed is either manual or metered. When a solvent/diluent blend is used, the resin is often first slurried in the diluent, containing about 20 percent solvent, and then the remaining solvent is added.

3.2.4 Solution PVC Applications

A summary of areas of usage is given in Table 3.2. PVC/VA copolymers are used mainly in paper, cardboard, foil, masonry, and metal coatings, and in can linings. The higher-molecular-weight, low-VA grades are useful in strippable coatings. Hydroxyl group-containing grades are used more widely because of their ability to crosslink with other resins. They are used in wood finishes, maintenance paints, can linings and magnetic tape binders, as well as in decorative paper and metal finishes. The carboxylated resins develop excellent adhesion to metal even without heat treatment, and are used for air-dried paints and finishes. Epoxy-modified resins are used mainly for can linings. High-VA grades (the Vinnol® 40 series) are useful in paints for concrete and road marking.

A typical wood finish could be based on about equal parts by weight (solids basis) of a hydroxyl-functional PVC/VA such as Ucar® VAGH, a butylated urea–formaldehyde resin, and a solution of an alkyd resin. The PVC/VA polymer would be dissolved at 20 percent solids in a 1:1 MIBK/toluene blend with pigment dispersion or gloss control agent. Additional solvent blend would then be added and the other resins mixed in. Prior to use, an alkyd drier catalyst would be added. A typical cure cycle would be 1 hour at 60 °C.

TABLE 3.2 Solution PVC Applications

UCAR Resin	Packaging		Metal Coating	Marine Coatings	Magnetic Media	Inks	Adhesives	Strippable Coatings	Wood Finishes
	Food	Other							
VYNS-3	×		×			×	×	×	
VYHH	×		×	×		×	×	×	
VYHD	×		×	×		×			
VMCH	×		×	×		×	×		
VMCC	×		×	×		×	×		
VMCA	×		×	×		×	×		
VERR-40	×								
VAGH	×		×	×	×	×	×		×
VAGD	×		×	×		×	×		×
VAGF		×	×	×	×	×	×		×
VAGC		×	×	×		×	×		×
VROH		×	×	×					×
Ucarmag 527					×				
Ucarmag 569					×	×			

A metal finish would usually be based on a carboxylated grade such as Ucar® VMCH or VYHH. For one-coat applications, a relatively slow-evaporating solvent blend would be used with 1–2 phr of a tin stabilizer. If pigmented, for example with 50–100 phr (solids basis) of titanium dioxide, 10–20 phr plasticizer, such as DIDP, would be added to achieve a useful coating viscosity and suitable film properties. About 5 phr of a liquid epoxy resin (e.g., Epon® 828) would be added to provide increased metal adhesion and crosslinking during cure cycles of 1–2 minutes at 200–225 °C. The above would be greatly facilitated by using a titanium dioxide liquid color dispersion in plasticizer.

A vinyl finish for ABS or ABS blends could be based on a 1:1 blend of a PVC/VA resin such as Ucar® VYHD and a carboxylated grade such as Ucar® VMCC (to promote increased adhesion) in a blend of MIBK and toluene, with the proportions adjustable to provide suitable drying times. Pigments would be added to the solution as liquid colors in plasticizer. After preparation at about 20 percent solids, the product could be thinned as needed for suitable coating weight.

Strippable coatings are typically based on PVC/VA resins such as Ucar® VYHH. Film properties can be adjusted by blending with a harder resin such as Ucar® VYNS-3, by adding plasticizer, or both. Release can be increased by addition of 2–5 phr of mineral oil. Pigmented transparent strippable film would use 1–2 phr of an organic pigment paste or liquid color, such as a phthalo blue or green. Opaque films would also use pigment dispersions. The final product commonly would be run at about 25 percent solids in an MEK/MIBK/toluene blend, with proportions so as to achieve useful coating viscosities and drying times.

Adhesives for PVC pipe joints typically use the high-molecular-weight grades of PVC/VA such as Ucar® VYNS-3 in very strong solvents such as cyclohexanone and tetrahydrofuran. Similar resins are used for films cast from solution, primarily for packaging applications.

3.3 CROSSLINKED PVC

In the 1960s, it was found that crosslinking thermoplastic low-density polyethylene (LDPE) led to notable improvements in heat aging, chemical, abrasion, deformation, and stresscracking resistance. Two methods were initially employed: crosslinking initiated by thermal decomposition of organic peroxides or by electron beam irradiation, both as sources of polymer radicals that could combine to form a carbon–carbon bond. Subsequently, it was found that vinyl or acrylyl organosilanes could be grafted to LDPE using traces of organic peroxide, typically in an extruder, and the product then crosslinked by contact with warm water, causing hydrolysis of alkoxy groups on silicon. The resultant Si–OH groups could then be condensed to Si–O–Si linkages with catalysts such as dibutyltin dilaurate or diacetate. All three methods are now in routine use to produce crosslinked PE wire coverings, heat shrink tubing, pipe, and coatings. Rated service temperatures for such articles notably exceed those for thermoplastic PE. In addition, filler compatibility is increased, a result of improved adhesive character.

The technology was applied to copolymers, such as ethylene vinyl acetate (EVA), and halogenated products such as CPE. It was natural to try to extend it to PVC. Thermal decomposition of organic peroxides in PVC leads to crosslinking, but also to rapid degradation and darkening. On the other hand, 50/50 blends of PVC and NBR can be peroxide-crosslinked, with adequate PVC stabilization, since NBR, which is completely compatible, reacts to crosslink faster than PVC degrades. The thermoset NBR traps PVC polymer chains—perhaps grafts to them. Typically, very little PVC can be solvent-extracted from these thermoset blends. Such compositions have been used for many years as hose covers and cable jackets. They have some advantage over competing materials such as chlorinated polyethylene (CPE), polychloroprene (Neoprene) (CR), and chlorosulfonated polyethylene (CSM) in terms of good color retention.

PVC/VA terpolymers containing unsaturated sites, such as with maleates, show fair response to peroxide crosslinking. Blends of EVA with such terpolymers have been used as the basis for thermoset wire insulations. It is also possible to use highly reactive unsaturated monomers as part or all of the plasticizer content and carry out peroxide cure. The products are usually dark from PVC degradation and have found little use in general purpose compounding.

A related technology involves production of foam, usually semirigid, from PVC containing another (not necessarily compatible) polymer that is readily crosslinked as an interpenetrating network (IPN). Originally urethane and urea resins were used. A major use is in small boat hulls as core materials, lending impact resistance, flexibility, flotation, and ease of application. Many other similar structural uses have surfaced. With sophisticated IPN components such as with aromatic polyamides and polyimides, a great range of service temperatures can be accommodated. Such products are used as thermal insulators in rockets and missiles. Leading suppliers include Alcan Airex (Airlite®) and DIAB Corp. (Divinylcell® and Klegecell®). Unfortunately, in the literature, these products tend to be referred to not as crosslinked polyvinyl chloride (XLPVC), but chlorinated PVC (CPVC), thus permitting confusion with CPVC designating chlorinated PVC.

3.3.1 Crosslinked Plastisols

The major area of use of peroxide-crosslinked PVC is that of plastisols. Part of the plasticizer, typically 5–15 phr, is replaced with a reactive multifunctional monomer. Crosslinking is developed during fusion by addition of low levels of organic peroxide, most commonly about 0.5 phr of 2,5-dimethyl-2,5-di-t-butylperoxyhexane (R.T. Vanderbilt, Varox®) in cycles of about 5 minutes at 200 °C. The crosslinked coatings have improved physical properties, particularly abrasion and chemical resistance. As a result, such products have found use in flooring topcoats. In cases where strong adhesion to a substrate such as glass or metal is desired, multifunctional acrylates are used. The most common examples are trimethylol propane triacrylate (Sartomer SR-351®, trimethylolpropane triacrylate (TMPTA)) and polyethylene glycol diacrylate (SR-344® PEGDA). The former yields a tighter cure, with maximum tensile strength, abrasion, and chemical resistance, and with an increase in hardness. The latter provides a more flexible crosslink, with higher elongation and lower build in hardness. Both provide improved adhesion to polar substrates.

In cases where high adhesion is not desired, such as with strippable coatings, methacrylates are used instead of acrylates. The highest levels of crosslink density, abrasion, and chemical resistance are obtained with trimethylolpropane trimethacrylate (SR-350® (TMPTMA)). This monomer also has fast response, but its tight cure increases hardness. This can be offset with additional plasticizer. Low-viscosity plastisols are obtained by using instead 1,3-butylene glycol dimethacrylate (SR-297® BGDMA) or hexanediol dimethacrylate (SR-239® 1,6-hexanediol dimethacrylate (HDDMA)). The latter also lends increased hydrophobic character to the coating.

Reactive monomers such as the above should be added shortly before use. They contain proprietary inhibitors to prevent premature reaction initiated by oxygen. The inhibitors are soluble antioxidants, which are themselves slowly oxidized and consumed. When ordering, it should be mentioned that the intended use is in PVC plastisol, so as to receive the appropriate grade. Methacrylate monomers are supplied by Ciba and Degussa, and methacrylate and acrylate monomers by Sartomer Corp.

3.3.2 Radiation-Crosslinked PVC

As peroxide crosslinking developed in the 1960s, there was a parallel advance in achieving thermoset products by irradiating the compound with electron beam generators. This was a result of development of large powerful sources, such as the Dynamitron® manufactured by Radiation Dynamics, Inc. Previously, sources, such as γ-ray swimming pool reactors and low-powered electron beams, provided sufficient energy input for high levels of crosslinking only after many hours of operation. This was not only inefficient and costly, but resulted in a great deal of polymer degradation as a side reaction. The electron beam accelerators developed in the past generation, using electrons energized from 400 kV to several million volts, enable crosslinking at speeds typically greater than line speeds in extrusion or calendering.

Whereas chemical crosslinking of PE yielded crosslink densities of 90 percent and more, electron beam processing tended to yield lower levels even at high doses (10–15 Mrad). This has been compensated for in two ways: by using medium-density instead of low-density PE, thus starting with better physical properties, and by using PE copolymers. It was found that EVA and acrylic copolymers crosslinked rapidly. It was also found that electron beam processing of CPE and CSM yielded excellent properties, in these cases often equal or superior to peroxide cure. Although electron beam processing heats the target, the effect is nowhere near that of steam continuous vulcanization (CV) temperatures (200 °C and higher). Thus, there is less side-reaction degradation of halogenated polymers. The natural extension was to experiment with PVC.

Early experiments at Bell Laboratories used 10–15 phr tetraethylene glycol dimethacrylate (TEGDMA) with DOP plasticizer in PVC and PVC/CPE blends with Ba/Cd stabilizers. These vulcanizates had good abrasion, cut-through, and crush resistance, but low elongation, poor color hold, and variable conductor adhesion. Use instead of linear phthalate plasticizers, lead stabilizers, and monomers such as TMPTMA led to a better balance of properties, with good color hold and easy conductor release. (It should be noted that if high conductor adhesion is desired, the monomer should be an acrylate rather than a methacrylate.)

Since fillers absorb ionizing radiation, they are often held to minimum levels. From this point of view, it would be preferable to use Ca/Zn or nonmetallic stabilizers rather than lead. To date, only one supplier of irradiated PVC wire coverings has announced lead-free products. Dosage is in the range of 5–10 Mrad and must be as uniform as possible. This is achieved by passing the insulated conductor under the electron beam many times, with radial partial rotation between passes. Irradiation of the product from a number of different directions compensates for variation of the effective dose with product thickness. Nevertheless, insulation wall thickness in this method is typically held to 1–2 mm or less. The greatest utility is therefore in control cable insulation and in wiring for electronic equipment, business machines, and appliances. Compared with thermoplastic PVC, the advantages are improved abrasion and crush resistance, tensile strength, and, above all, resistance to melting if contacted by a soldering iron. Elongation and flexibility are somewhat reduced. The extent of crosslinking in commercial products (35–50 percent) generally does not permit an increase in service temperature rating. Irradiated PVC wire coverings are rated for 90 and 105 °C service.

Suitable compounds are sold by, among others, Dow Chemical—for example DFDA-6530®, for control cable insulation. The Dow products do not use lead stabilizers. Offshore suppliers include Zhonglian (e.g., 0531X 105 C compound). Such compounds do well in 136 °C heat aging, retaining more than 70 percent of initial elongation (150–200 percent) after 168 hours. Typical extrusion conditions are barrel 140–160–170–175 °C, head and die 170–180 °C. A typical compound for automotive wire could contain 10–20 phr $CaCO_3$, 50–60 phr TOTM or TINTM, 5–6 phr tribasic lead sulfate, and 10 phr TMPTMA. It would be crosslinked subsequent to extrusion by doses of 5–8 Mrad. Electronic hookup wire for ratings to 105C UL 1430 and 3317, CSA 90C RR-64, and 105C REW, both for 300 V service, and for 105C MIL-W-16878, 1000 V, would use electrical-grade calcined clay at low loadings in preference to $CaCO_3$. The clay can be silane-treated for higher modulus and crush resistance, in which case vinyl or acrylic silanes are used, typically at 1–2 percent of the clay content. Low levels of antioxidant (e.g., 0.1 phr) are used. These should be restricted to those resistant to irradiation (see Section 4.1.3) such as Irganox® 1010.

Typical products are supplied by Rockbestos Suprenant Cable under the trade name Irravin® C. Another area of use is with very small wires inside of cameras and similar equipment. A range of suitable products is supplied by Sumitomo Cable under the trade name Irrax®.

3.3.3 Silane-Crosslinked PVC

When crosslinking is carried out by irradiation or thermal decomposition of organic peroxides, silanes of the type $CH_2{=}CH{-}Si{-}(OR)_3$ or $CH_2{=}CH{-}CH_2{-}Si{-}(OR)_3$ (i.e., vinyl or acrylyl silanes), can be reacted with fillers having surface

—OH groups and then bonded to the polymer during the free-radical crosslinking process. In such cases, the silane is added to the filler during mixing, or a pretreated filler is used. In silane crosslinking of PVC, an amino- or mercaptosilane, most often a trimethoxysilane, is reacted with the polymer:

$$
\begin{aligned}
&(\mathrm{RO})_3\text{—Si—R}' - \mathrm{NH_2} + \text{—CH}_2\text{—CHCl}- \\
&\quad \rightarrow \text{—CH}_2\text{—CH—NH—R}'\text{—Si—}(\mathrm{OR})_3 + \mathrm{HCl} \\
&(\mathrm{RO})_3\text{—Si—R}'\text{—SH} + \text{—CH}_2\text{CHCl—} \\
&\quad \rightarrow \text{—CH}_2\text{—CH—S—R}'\text{—Si—}(\mathrm{OR})_3 + \mathrm{HCl}
\end{aligned}
$$

After processing, the product, which contains a hydrolysis catalyst (usually DBTDL or DBTDAc), is contacted with warm water, converting the Si—OR groups at least partially to Si—OH. These then condense to form highly stable Si—O—Si crosslinks. Trimethoxysilanes are the most reactive and are generally used; triethoxysilanes can be used, but require longer hydrolysis times. Since the product is often allowed to stand in water for 24 hours, a high extent of reaction is achieved, with crosslink densities higher than with irradiation.

With this process, it is important not to use up Si—OR linkages by reaction with filler surfaces. This tends to preclude the use of clay and silica, and also of hydrous fillers, although it is possible to overcome the side reaction by use of sufficient silane. Useful fillers include pH-neutral carbon blacks (e.g., MT) and refined grades of $\mathrm{CaCO_3}$. Similarly, additives with active hydrogen, such as stearic acid, must be avoided. The Pb—OH groups on lead stabilizers are not a problem. Suitable compounds are available from Dow Chemical under the designations DFDA-5400 and 5401.

Although the technology associated with PVC latex, solution PVC, and crosslinked PVC applies to a minor fraction of worldwide PVC usage, it is interesting and often ingenious, and thus well worth perusal by all plastics technologists on the grounds that the approaches used may suggest innovations in other areas.

CHAPTER 4

Antidegradants

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4.1 USE OF ANTIOXIDANTS IN PVC

A great deal has been written about how PVC degrades. The extent of theorizing as to the details of the reactions involved far exceeds the data collected. There are differing schools of thought and disputation. It is the aim of this chapter to avoid such exercise in favor of presenting the facts, as currently known, that will aid the formulator in devising the best compound for the application. Current use and recommendations are provided and explanations framed so that the formulator has a basis for innovation beyond what is current.

The inhibition of degradation of PVC during processing is the function of the stabilization system. Prevention of degradation during the service life of the manufactured article, and during accelerated tests carried out to demonstrate a satisfactory service life, almost always requires both stabilizer and antioxidant. PVC articles are highly durable. They can persist indefinitely in landfills (there are, in fact, additives to counteract this durability). Nevertheless, almost every PVC compound contains at least one antioxidant. These may be added knowingly or through use of stabilizers or plasticizers that typically contain antioxidants. If PVC resin is dissolved in a suitable solvent and air is bubbled through at room temperature, oxygen uptake is relatively slow. During processing and service, however, PVC eliminates hydrogen chloride (HCl), developing unsaturation. The resultant HCl catalyzes further elimination before escaping, leading to conjugated (—C=C—C=C—) unsaturation. Such structures are highly prone to oxidation. If a solution of a hydrocarbon with extensive conjugated unsaturation, for example, β-carotene, is exposed to air at room temperature, oxygen uptake is immediately noted. The bond energy of a C—H group adjacent to unsaturation (—C=C—C—H) is relatively low. As the number of conjugated double bonds increases, allylic C—H bond energy progressively drops, facilitating proton loss in initiation of oxidation:

$$\text{—C=C—C—H} + O_2 \rightarrow \text{—C=C—C}^{\bullet} + {}^{\bullet}\text{OOH} \qquad (1)$$

Free radicals may also result from carbon–carbon bond breaking from shear during processing:

$$\text{—C—C—} \rightarrow \text{—C}^{\bullet} + {}^{\bullet}\text{C—} \qquad (2)$$

In the absence of stress, Reaction (2) reverses, bond formation being exothermic and thus favored, provided reaction with oxygen (Reaction 3) does not occur first:

$$—\mathrm{C}^{\bullet} + \mathrm{O}_2 \rightarrow —\mathrm{COO}^{\bullet} \tag{3}$$

$$—\mathrm{COO}^{\bullet} + —\mathrm{CH} \rightarrow —\mathrm{CO—OH} + —\mathrm{C}^{\bullet} \tag{4}$$

Reaction (3) is rapid at processing temperatures, and the peroxy radical that is formed can easily abstract a proton from an activated source such as —C=C—CH, as in Reaction (4), creating a chain reaction. This is not in itself calamitous, since chain reactions that yield merely one free radical per starting radical usually fail to propagate from losses in side reactions. At elevated temperatures, however, the product of Reaction (4), a hydroperoxide, will decompose:

$$—\mathrm{CO—OH} \rightarrow —\mathrm{CO}^{\bullet} + {}^{\bullet}\mathrm{OH} \tag{5}$$

Both of the products of Reaction (5) can abstract protons from the polymer as in Reaction (4), greatly facilitating the chain reaction. Reaction (5) is, in addition, catalyzed by a number of metals having oxidation states separated by one electron (Fe, Cu, Ni, Mn, Co, V, Ti, and others).

The consequences of the above series of reactions are profound. One is that the polymer is increasingly subject to further oxidation. Another is that the radicals formed may fragment. This (chain scission) cuts molecular weight and viscosity. Alternatively, radicals from two polymer chains may combine to form a crosslink. In degradation of PVC, early chain scission is followed by crosslinking. Both seriously interfere with processing. In addition, the development of oxygenated groups increases color, particularly in combination with unsaturation from HCl loss. The picture of a chain reaction with high yield leading to a series of disastrous results seems daunting. But it is not. Chain reactions can be disturbed using low levels of the right additives; that is, they are interference-sensitive. If oxidation were not a chain reaction, much higher levels of antioxidants would be needed.

4.1.1 Primary Antioxidants

A common supposition is that antioxidants are sacrificially oxidized to protect the polymer (or other sensitive ingredient, such as food). Eventually, the antioxidant (A/O) is, of course, oxidized, but that is not its main purpose. It is intended to complex polymer radicals:

$$—\mathrm{C}^{\bullet} + \mathrm{A/O} \rightarrow [—\mathrm{C} \rightarrow \mathrm{A/O}]\ \text{complex} \tag{6}$$

$$—\mathrm{CO—O}^{\bullet} + \mathrm{A/O} \rightarrow [—\mathrm{CO—O} \rightarrow \mathrm{A/O}] \tag{7}$$

It is anticipated that the complexes formed in Reactions (6) and (7) will persist long enough to dissipate energy as heat, and then reverse. The lower-energy radicals that are returned will react, but merely slowing them down tends to defeat the chain feature of the reaction. In these reactions, the antioxidant acts as a reverse catalyst—an additive that promotes driving the reaction to the left—without being consumed. An immediate consequence is that an antioxidant can act more than once. In fact, at the levels at which they are usually employed, it must. Additives that function in this way are primary antioxidants.

Radicals readily form complexes with aromatic compounds rich in electron density. The electron-deficient orbital (with only one electron) overlaps the aromatic π-cloud. The most active species are aromatic amines and phenols. In order to prevent reactions that would consume the antioxidant, the *ortho* and *para* positions on the ring are blocked with substituents. These are electron-donating, to increase the electron density of the ring, chiefly alkyl groups. Most often t-butyl groups are used as the *ortho* substituents, so as to hinder sterically oxidation of the amino or phenolic group. The *para* position typically is substituted with a larger group that limits volatility and also provides compatibility with the polymer. The most common starting material for synthesis is 2,6-di-t-butylphenol, readily available through direct alkylation of phenol with an aluminum catalyst. It then may be further alkylated in the *para* position by reaction with activated double bonds (or electrophilic reagents generally).

The radical with which the formulator is most concerned is oxygen ($^\bullet O{=}O^\bullet$), a diradical. It is likely that it complexes rapidly with antioxidants, that this is the role of the latter in antioxidation, functioning as a phase transfer reverse catalyst:

$$[\text{—C}^\bullet \rightarrow \text{A/O} \leftarrow \text{O}_2] \rightarrow \text{—C}^\bullet(\text{slow}) + \text{A/O} + \text{O}_2 \qquad (8)$$

In due course, Reaction (9), oxidation of the antioxidant, will also occur:

$$[\text{—C}^\bullet \rightarrow \text{A/O} \leftarrow \text{O}_2] \rightarrow \text{—COOH} + \text{A/O}^\bullet \qquad (9)$$

that is, a proton will transfer from the antioxidant. Although the formulator will try to maximize the competitiveness of Reaction (8), Reaction (9) cannot be totally avoided. Reaction (9) is favored by increasing temperature, thus minimizing the advantage of Reaction (8) of lower activation energy, by increased shear, initiating more radical sites, and by oxygen concentration (aerobic exposure during processing). Reaction (8) is favored by increased antioxidant level and milder processing conditions; that is, in effect by increased overall cost. Fortunately, the formulator has further tools in his or her kit.

4.1.2 Secondary Antioxidants

The most damaging feature of oxidation is Reaction (5), in which the yield of active radicals is increased to greater than one-for-one by hydroperoxide decomposition. Hydroperoxides may, however, be decomposed by other than free-radical routes. Two species that assist are organophosphites and thio compounds, as in Reactions (10) and (11):

$$\text{—C—OOH} + (\text{RO})_3\text{P} \rightarrow \text{—C—OH} + (\text{RO})_3\text{P{=}O} \qquad (10)$$

$$\text{—C—OOH} + \text{R}_2\text{S} \rightarrow \text{—C—OH} + \text{R}_2\text{S{=}O} \qquad (11)$$

In these reactions, the additives are sacrificed through oxidation. The other product is an alcohol, a group ordinarily more difficult to oxidize than activated C—H. With many phosphite esters, Reaction (10) is very fast, leading to a high level of protection during processing. Thio compounds, such as dilauryl or distearyl thiodipropionate (DLTDP, DSTDP) have many regulatory approvals and provide protection during service life. (Unfortunately the two types of additive react and are rarely used in the same recipe.) Hydroperoxide decomposition is the characteristic that has led to the term "secondary antioxidant." It is likely, however, that primary (hindered phenols) and secondary antioxidants complex and that it is the combination that provides multiple modes of defense. This is taken advantage of in several commercial products where the "R" groups in the organophosphite are phenolic antioxidant residues.

Both of the above types of secondary stabilizer react with unsaturated carbonyl compounds formed by resin oxidation, limiting discoloration. Possibly their most useful function, however, is in defeating Reaction (9) above, the loss of primary antioxidant by its oxidation. This is again sacrificial:

$$[\text{—C}^{\bullet} \rightarrow \text{A/O} \leftarrow \text{O}_2] + (\text{RO})_3\text{P} \rightarrow \text{—CO}^{\bullet} + (\text{RO})_3\text{P=O} + \text{A/O} \tag{12}$$

$$[\text{—C}^{\bullet} \rightarrow \text{A/O} \leftarrow \text{O}_2] + \text{R}_2\text{S} \rightarrow \text{—CO}^{\bullet} + \text{R}_2\text{S=O} + \text{A/O} \tag{13}$$

Since the goal of the formulator is repeated function of the primary stabilizer and in its protective reactions the secondary stabilizer is consumed, clearly the latter must be used at a higher level. This is almost invariably the case in PVC compounds.

4.1.3 Choice of Antioxidants

Probably the most prevalent antioxidant in worldwide use is the *para*-methyl derivative of 2,6-di-t-butylphenol, BHT (here abbreviated as A/O—CH_3). BHT is low-cost and fast-acting (highly mobile), and has many regulatory approvals. It has been used in (or with) organotin and calcium/zinc stabilizers for food contact and medical applications. BHT is volatile and inappropriate for service at elevated temperatures. It reacts rapidly with oxides of nitrogen, leading to discoloration and is thus unsuitable for outdoor use. The most pervasive problem is its oxidation:

$$2\text{A/O—CH}_3 + \text{O}_2 \rightarrow \text{A/O—CH=CH—A/O} + 2\text{H}_2\text{O} \tag{14}$$

The dimer formed is rapidly oxidized to a quinone having a bright yellow color whose intensity is increased by coordination to metals such as titanium. BHT was at one time often used as the antioxidant in plasticizers, but has been largely superseded. It should be used in PVC only in formulations where it has been specified by regulatory approval and in which it would be impractical to seek new sanctions. No data has surfaced from which it can be concluded that BHT is a human or environmental hazard. It must be anticipated, nevertheless, that there may be persons allergic or hypersensitive to it, as there are to almost all additives. BHT is available from Ashland Chemical, Bayer, Chemtura, PMC, UOP, and others.

In the past, the most widely used antioxidant in PVC was 2,2-bis-(p-hydroxyphenyl)propane (bisphenol A, BPA). Although it is often shown in textbooks with both aromatic rings in the plane of the paper, suggesting that it is not a hindered phenol, three-dimensional scale models show that aromatic protons from one ring can interfere with easy attack of the phenolic group of the other. One major use was in flexible PVC compounds that used barium/cadmium stabilizers. BPA served as an antioxidant not only for polymer and plasticizer, but also for the metal carboxylates in powder stabilizers based on laurates and stearates. With liquid barium/cadmium stabilizers based on barium nonylphenate (or other phenolate) it was generally not needed. When the primary metal of the stabilizer is zinc rather than cadmium, the use of BPA is appropriate only in black or dark-colored compounds. In the presence of strong Lewis acids such as traces of zinc chloride, the oxidation product(s) of BPA are condensed into dark chromophores, probably involving dimerization as with BHT. This is particularly the case where zinc compounds are used to activate azodicarbonamide blowing agent.

The other major area of use is in lead-stabilized wire coverings that require only modest loss of elongation after accelerated heat aging tests. Elongation is lost because of two factors: volatilization of plasticizer and oxidative degradation (of resin and plasticizer). No antioxidant can compensate for a completely inappropriate choice of plasticizer. Nevertheless, use of 0.25–0.5 parts per 100 of resin (phr) of BPA can enable a broader plasticizer choice—often more than offsetting the cost of the antioxidant. When a lead stabilizer is replaced with barium/zinc or calcium/zinc, BPA should be retained only in black. In other colors, use should be made of antioxidants with low zinc sensitivity.

Although BPA may be an endocrine disrupter (estrogen mimic) at high dosage in mice and rats, there is at present no evidence of such effects in humans at anticipated exposure levels, or of environmental hazard. Again, it must be anticipated that there will be occasional hypersensitive persons. Both BHT and BPA are Food and Drug Administration (FDA) sanctioned as Generally Recognized As Safe (21CFR175.105). BPA is available from Aristech, Ashland, Mitsui, Shell Chemicals and others.

An antioxidant used in tin-stabilized rigid PVC topcoat layers for outdoor applications is octadecyl 3,5-di-t-butyl-4-hydroxyhydrocinnamate, abbreviated as per the above convention as $A/O{-}CH_2CH_2CO_2C_{18}H_{37}$ (A/O designating di-t-butylphenol). It is sold under the trade names Irganox® 1076 (Ciba-Geigy), Ultranox® 276 (Chemtura), Ethanox® 376 (Albemarle), Arenox® A-76 (Reagens), *inter alia.* The octadecyl "tail" provides good mobility in a rigid matrix. Mobile complexes with lubricants are likely. The oxidation products of this additive tend to be colorless. It should be one of the top choices for siding and profile topcoats, typically at levels of 0.1–0.2 phr. There is no evidence of negative health or environmental effects with this antioxidant and, as with BHT and BPA, which it has replaced in many applications, there is FDA sanction for its use 21CFR178.2010, in rigid PVC up to 0.2 percent and in rigid and semirigid, per 178.3790, to 0.05 percent. Another appropriate application is in blends with less polar polymers such as EVA (in which it is also an excellent antioxidant).

Probably the most widely used antioxidant in plastics is tetrakis[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane, abbreviated as per the above convention as (A/O—$CH_2CH_2CO_2CH_2)_4C$. It is sold under the trade names of Irganox® 1010 (Ciba-Geigy), Ethanox® 310 (Albemarle), Arenox® A-10 (Reagens), *inter alia*. This additive is excellent in PVC blends both with polar and with less polar polymers. There are, in addition to replacing BHT and BPA, two applications where its use predominates. One is in PVC articles that are subject to sterilization by irradiation. Typical doses are in the range of 25–40 kilograys (kGy, 1 kGy = 100,000 rads) for medical instruments and 1–7.5 kGy for food packages (the lower figure for fruits and vegetables and the higher for meat). These levels destroy common (e.g., *Salmonella*) and pestilential (e.g., *Vibrio cholerae*) contaminants. Highly resistant spores (e.g., anthrax) may require lethal doses of as much as 20 kGy. As long as electron beam or γ-radiation is consumed in microbial destruction, little damage to the composition is likely. To insure a sterile product, the exposure is often greatly in excess of this. The energy delivered during irradiation is sufficient to overcome the activation energy barrier to oxidation of a hindered phenol or of its complex with a polymer radical. In irradiation, the phenolic group is, therefore, sacrificial. This antioxidant can sacrifice more than one phenolic group and persist to function in prolonging service life. When present in flexible or semirigid PVC compositions, use of phosphites as secondary antioxidants with Irganox® 1010 leads to good color retention. The other major use is related: inclusion as the antioxidant in compositions to be crosslinked by electron beam radiation. Other antioxidants that have been used successfully include Ethanox® 330 (Albemarle) and Vanox® GT (Vanderbilt). Irganox® 1010 and chemical equivalents have FDA sanction per 21CFR175.2010, as does Vanox® GT and its equivalent, Ethanox® 314, to 0.5 percent in all polymers for indirect food contact in packaging. When exposure to radiation is expected, use level should be increased to the range of 0.15–0.3 phr, since antioxidants already present in the plasticizer may not be suitable. In addition, epoxidized oils are subject to damage and may yield products of unacceptable taste and odor if inadequately protected.

In plastisols, often the phosphite content provides adequate protection. If this is not the case, sometimes with long fusing cycles, it is convenient to use a liquid hindered phenol added to the plasticizer. An example is 2,6-di-t-butyl-4-s-butylphenol, A/O—$CH(CH_3)CH_2CH_3$, Vanox® 1320 (Vanderbilt). It is about as fast-acting as BHT, FDA sanctioned per 21CFR175.105, less volatile, and less prone to forming colored oxidation products. Another liquid product useful in this regard is Irganox® 1135, A/O—$CH_2CH_2CO_2C_8H_{17}$. Both were used also as additives to circulating water/ethylene glycol in crosslinked NBR/PVC floor and driveway heater hose as a repair measure to counteract hardening during service.[1] The possibility of having additives absorbed to repair the composition subsequent to manufacture is not common, but should not be totally discounted.

An antioxidant widely used in recent barium/zinc- and calcium/zinc-stabilized PVC compositions is 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, Topanol® CA (AstraZeneca). This antioxidant has three hindered phenolic groups linked in the *para* position to the butane chain. Each has a t-butyl group *ortho* to the phenol, but has a methyl group, not in the other *ortho* position, but *meta* to the phenol. This leaves a more or less unblocked activated *ortho* C—H. This structure permits the antioxidant to act both in a repetitive and in a sacrificial mode, which is possibly key to its widespread applicability. Topanol® CA has FDA sanction per 21CFR178.2010. With (or in) barium/zinc and calcium/zinc stabilizers, typical use is in the range of 0.05–0.2 phr. With phosphite secondary antioxidants, color retention is excellent. Topanol® CA may also be used in place of BPA in lead stabilized wire insulation, with the advantage that one-third to one-half as much is needed for equivalent retention of elongation after heat aging. For retention of electrical properties during exposure to hot water, the lower the use level of additives, the better. This antioxidant is also effective in blends of PVC with other polymers, and has been used in rigid compounds stabilized with organotin carboxylates. It has also been used in applications involving irradiation.

Antioxidant effectiveness depends on several factors. Mobility within the compound is important, but is often accompanied by volatility. BHT, for example, is highly mobile and fast-acting, but too volatile for applications involving extended aerobic processing, such as calendering, or those requiring severe accelerated aging tests, as with wire insulation. It is much preferable to achieve mobility by using a larger molecule with a built-in nonpolar tail, such as Irganox® 1076, or to use lubricants that can complex lubricants such as Irganox® 1010 or Topanol® CA, improving their mobile capacity. Ester lubricants are particularly good in this respect.

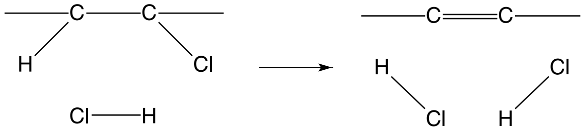
Uniformity of antioxidant level can be a problem when the use level is very low compared with other ingredients. This potential source of variability can be minimized by having the antioxidant as one of the components of the stabilizer. This option is simple with powdered mixed metal stabilizers. It also provides antioxidant protection for stearate or laurate salts of primary and secondary metals. With liquid mixed metal stabilizers, particularly those that are solvent-free and contain overbased metals, there may be compatibility problems. Irganox® 1076 is often used in such systems. Multifunctional ingredients can decrease (or destroy) shelf stability of overbased liquid stabilizers. Nevertheless, with suitable use of compatibilizing agents, antioxidants such as Topanol® CA and Irganox® 1010 have been used routinely in liquid stabilizers. Although liquid organotin stabilizers usually contain antioxidants, the levels used tend to provide protection only for the stabilizer itself. BHT has been largely replaced by newer antioxidants in tin stabilizers. For service protection, as in siding and window profile topcoats, additional antioxidant should be added, not only to protect the polymer but also the UV light absorber. If the level poses weighing and incorporation problems, the antioxidant can be added as a concentrate, in filler for addition during blending, or in resin, pelletized for addition at the extruder, perhaps combined with color concentrate. In antioxidant selection, the worst possible choices are those made with materials cost as the most important criterion. The effect of poor performance in the field is to reinforce the competitive position of alternatives to vinyl.

4.2 HEAT STABILIZERS

With polymers that are capable of eliminating small molecules from the action of heat, shear, UV light, or ionizing radiation, this is usually the first degradative step. This group includes not only PVC, but also CPE, polychloroprene (CR, Neoprene), chlorosulfonated polyethylene (CSM, Hypalon®), polyepichlorohydrin (ECO), polyvinyl acetate (PVAc), and several fluoropolymers (e.g., FKM). With all except PVC, the elimination of hydrogen halides (usually HCl) can be controlled by use of reactive basic ingredients, such as magnesium or lead oxide. MgO is routinely used in Neoprene, Hypalon®, and Viton®. If a weak acid, such as acetic, is given off, as with PVAC and, in some cases, EVA, it may be scavenged by low levels of a strong receptor, typically polycarbodiimide (PCD, Bayer Stabaxol® P). These additives are insufficient to stabilize PVC effectively. That is not to say that alkaline additives do not increase stability—they may well—but few PVC compositions can rely on their use as primary stabilizers. Even a weak base such as calcium carbonate will have a secondary stabilizing effect. This is the main reason that unfilled compounds are often harder to stabilize and commonly use higher levels of heat stabilizers than those with calcium carbonate filler. On the other hand, very high levels of calcium carbonate, as in floor tile or cove base, often require high stabilizer levels because of their physical interference with stabilizer mobility.

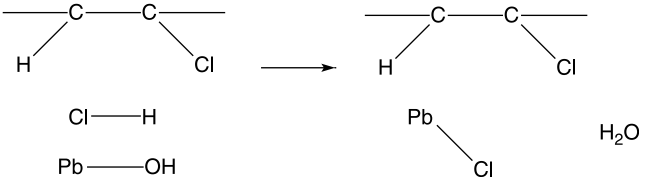
Of the above polymers, only PVC has a sufficiently regular structure to "unzip" HCl to a conjugated polyene, the HCl of elimination catalyzing further elimination before escaping, leading to a string of conjugated double bonds. The work of Fisch, Bacaloglu and colleagues[2] has established the chain reaction character of this initial step. As with oxidation, this is not necessarily a bad feature. The polymers mentioned above that do not "unzip" commonly use high levels of acid absorbers, in some cases as high as 15–30 phr. Fortunately for the user (if not for the stabilizer supplier), PVC stabilizers can be used at much lower levels. This is a consequence of chain reactions being simpler to disrupt (if the stabilizing additives are chosen carefully). PVC stabilizers have two main functions: to direct (most of the) eliminated HCl to more or less harmless locations before it can initiate unzipping; and to deactivate sites on the polymer, most often allylic —Cl, inhibiting HCl elimination. The stabilizer may also promote *cis–trans* isomerization of polyenes formed by HCl elimination and may have secondary functions in lubrication, air release in plastisols, activation of blowing agents in chemically foamed products, control of surface energy in printable films, *inter alia*.

Both of the major functions seem not at all simple. How is a stabilizer to trap a small, fast-moving molecule such as HCl before it can reach a nearby site and catalyze elimination of a second HCl as in Reaction (15)?



(15)

Even unwieldy stabilizers such as tribasic lead sulfate, probably an inorganic low polymer, seem able to do this at low levels with remarkable efficiency (under reasonable processing conditions). The answer is that the stabilizer is already at the degradation site. The latter is most often an allylic C—Cl. The allylic group [—CH=CH—C(Cl)—] has C=C absorption in the infrared distinct from isolated olefinic bonds that are not conjugated with —Cl. In equimolar mixtures of model allylic compounds with PVC stabilizers of all types, the C=C infrared absorption is shifted back to that of an isolated double bond.[3] Thus (at least in model compounds) the stabilizer has deactivated activated sites. This is its first purpose, and under more or less mild processing or service conditions may be the main effect. It is analogous to the antioxidant's first-step function of reversing the initiation of oxidation. With sufficient stress input, this protective effect will be overcome, HCl will emerge from the site, but directly into the grip of the stabilizer. The latter, as mentioned above, will function so as to direct HCl to an innocuous end, often as calcium or barium chloride, or the chlorides of hydrous zeolite or hydrotalcite, or those of lead-based stabilizers.



(16)

In Reaction (16), a lead stabilizer is shown at the degradation site interfering with HCl-catalyzed elimination (Reaction 15). It could as readily be a mixed metal complex or a complex of organotin stabilizer with calcium stearate.

The second main reaction of stabilizers, the replacement of labile chloride (—CH=CH—C—Cl) by ligands from the stabilizer, is no longer thought surprising since the pioneering work of Frye and Horst,[4] which demonstrated that carboxylate groups are transferred from mixed metal stabilizers to the polymer. Consider Reaction (15) in which the —Cl on the polymer chain has been replaced with a bulky laurate or stearate group. Elimination of the elements of lauric or stearic acid is not impossible, but requires increased energy input and, most importantly, is unlikely to involve a chain reaction. Labile chloride replacement by mixed metal stabilizers, for example, a blend of calcium stearate ($CaSt_2$) and zinc stearate ($ZnSt_2$), is most often found in textbooks as a two-step reaction even though intermediates such as mixed chlorostearates have never been isolated. Kinetic evidence suggests the mechanism is instead concerted:[5]

$$—C{=}C—C—Cl + ZnSt_2 \rightarrow St—C—C{=}C— + Zn(Cl)St \tag{17}$$

$$Zn(Cl)St + CaSt_2 \rightarrow ZnSt_2 + Ca(Cl)St \tag{18}$$

A concerted mechanism (one of the possibilities suggested by Frye and Horst) would involve a mixed metal complex, probably carboxylate-bridged, which might be represented as $\text{St—Zn—(St)}_2\text{—Ca—St}$. Molecular models of a carboxylate-bridged complex and a section of polymer containing an allylic group show that if calcium is brought into proximity of the allylic —Cl (carbon 1), then stearate on zinc is in position to displace at carbon 3 simultaneously:

$$\begin{gathered}\text{C(3)=C(2)—C(1)—Cl}\\ \text{St—Zn—(St)}_2\text{—Ca—St}\end{gathered}$$

The two metals could as easily be barium and cadmium or barium and zinc. In the case of lead stabilizers, the work of Michell and colleagues[6] has shown that the two metals are lead and lead; that is, that lead stabilizers, in the presence of stearic acid, displace labile chloride allylically, most likely with chloride being transferred to a different lead atom, replacing —OH, as in Reaction (19):

$$\begin{gathered}\text{—C=C—C—Cl} + \text{St—Pb—[\ \ ]—Pb—OH} \rightarrow\\ \text{St—C—C=C—} + \text{HO—Pb[\ \ ]—Pb—Cl}\end{gathered} \tag{19}$$

It seems probable that in stabilization systems based on combinations of organotins and calcium stearate, a complex of the two additives displaces labile chloride with a ligand from tin, either carboxylate or mercaptide, at carbon 3, with chloride from carbon 1 going to calcium. This may be a concerted reaction, (i.e., occur simultaneously), or the tin stabilizer may function as a phase transfer catalyst for transfer of chloride to calcium stearate, stearate replacing the tin ligand that has been lost, as in Reaction (20):

$$\text{—C=C—C—Cl} + \text{[Sn—R]} + \text{CaSt}_2 \rightarrow \text{R—C—C=C—} + \text{[Sn—St]} + \text{Ca(Cl)St} \tag{20}$$

When tin-stabilized products that have been processed without evident degradation are examined for reaction products, essentially all chloride not in the PVC polymer is found as calcium chloride, or the chlorides of hydrotalcite or zeolite, if these are used as costabilizers. In a sense, therefore, all stabilizers are mixed metal systems. (It should be noted that the term "stabilizer" is popularly used to designate not only additives that scavenge small molecules, but (often by suppliers) to mean antioxidants, packages of antioxidants and other ingredients, and UV light absorbers; that is, anything with a protective effect, presumably adding cachet to the product.) In the PVC industry, it usually denotes an additive that performs the main functions described above, although very often containing one or more antioxidants.

4.2.1 Lead Stabilizers

The oldest heat stabilizers used in PVC are those based on lead. Tribasic lead sulfate is thought to be the most widely used PVC stabilizer worldwide. This is based on its low cost, great effectiveness in providing long failure time both in rigid and flexible compounds, and formation of reaction products that are not hygroscopic. It is described in many literature sources as $3PbO \cdot PbSO_4 \cdot H_2O$. This is an oversimplification, similar to describing clay as a double compound of aluminum and silicon oxides. The infrared spectra of lead stabilizers, published in 1977, indicate the presence of Pb—OH, not of water.[7] A more informative description would be $[—(—O—Pb—O—)_2SO(—O—Pb—OH)_2—]_n$. This emphasizes that it is an inorganic "polymer" with covalent bonding, and has two active Pb—OH groups. Such an assignment is consistent with X-ray diffraction[8] and NMR[9] data. Reaction with HCl leads to the product $(—O—Pb—O—)_2SO(—O—Pb—Cl)_2$. This chloride has very much lower water solubility than lead dichloride and underlies the use of the stabilizer in products such as wire insulation, roofing, and pond liner.[10] Tribasic lead sulfate appears to be used exclusively in PVC compounds, usually at a level of 4–5 phr, although this may be reduced with optimum choice of resin and plasticizer. It is produced in North America as Halbase® 10 (Halstab), addiBase® (Addenda), and Demostab® P-70 (Demosa), and has been imported as Naftovin® T3 (Chemson) and Baerostab® V 220 MC (Baerlocher).

Tribasic lead sulfate is the most prevalent product of the reaction of litharge with sulfuric acid, generally run with traces of formic or acetic acid as catalyst. It is carried out commercially in water suspension or in bulk with continuous agitation. In either case, the product, whose natural crystalline shape is needle-like, is ground to a fine powder. It may then be coated with stearic acid, barium, calcium, or lead stearate in order to promote stearate displacement of labile chloride (leading to improved color retention), and/or bisphenol A antioxidant. Grades for use in rigid PVC, where its use continues in parts of the world, may be coated with cadmium stearate to minimize sulfur stain. Cadmium stearate is also used for the same purpose in crosslinked nonblack NBR/PVC cable jackets and hose covers that are oven vulcanized inside a lead sheath. Although CdS is more soluble than PbS, cadmium is more reactive towards sulfur, thus forming a yellow rather than a black product.

With care, the above reaction may be directed towards formation of monobasic lead sulfate: $PbO \cdot PbSO_4$ in textbooks, but more likely $—(—Pb—O—)_2SO_2—$.[9] Monobasic lead sulfate (addiBase® Mono) is a poor PVC stabilizer but a quite good white pigment, often mixed with basic lead carbonate in white lead recipes. Under other reaction conditions, one can prepare tetrabasic lead sulfate, likely $(O—Pb—O)_3S(O—Pb—OH)_2$.[9] This product is a good stabilizer, often providing longer failure time than tribasic lead sulfate, but its use leads to darkening under UV light exposure with formation of colloidal PbO. It is used in Europe in black or dark colored cable jackets. In the United States, it has found use in battery plates in place of litharge. It is produced domestically by Halstab® and Addenda (addiBase® Tetra) and imported by Chemson (Naftovin® T11) and Baerlocher (Baerostab® V 420 MC). Normal lead sulfate, $PbSO_4$, has no value other than as a dense filler.

The course of the reaction can be followed by tracking pH to monitor the consumption of sulfuric acid, and by color. In all its crystalline forms, litharge is distinctively colored, resulting from electronic transition from the electron pair in Pb(II) to a vacant orbital on a nearby lead atom. As stabilizer is formed, the increase in Pb—Pb distance shifts light absorption out of the visible into the ultraviolet (leading to a certain amount of UV light protection). Monobasic and tribasic lead sulfates are white, tetrabasic, off-white, or cream-colored. In both tribasic and tetrabasic, proton nuclear magnetic resonance (NMR) absorption from —OH is split into two equal peaks, suggesting two Pb—OH groups in fairly close proximity. This is borne out by diffraction studies. Although the exact configuration of a stabilizer-degrading site complex cannot be drawn with any certainty, if one makes models of the site and of a lead stabilizer, it is possible to visualize the shielding effect of the latter towards HCl approach to the potential degradation site.

A related product is dibasic lead phosphite: $2PbO \cdot PbHPO_3 \cdot ½\,H_2O$ in textbooks, but probably $[\text{—O—Pb—O—PH(O—Pb—OH)}_2\text{—}]_n$. The NMR spectrum shows not water, but —OH and P—H protons in a molar ratio of 2 : 1, and its structure appears to be similar to that of tribasic lead sulfate.[9] Dibasic lead phosphite also forms a dichloride on reaction with HCl, but is also usually oxidized, the P—H bond converted to P═O. It is a combination stabilizer and phosphite antioxidant. This has led to usage in the United States in PVC roofing, pond liner, and nonblack electrical products, such as yellow tape. In areas of the world where tribasic lead sulfate is used in rigid PVC, combinations of sulfate and phosphite, often 2 : 1, are common. Usage levels are the same as tribasic lead sulfate, 4–5 phr. Dibasic lead phosphite is also used, at higher levels, as a water-resistant combination hydrogen halide absorber/antioxidant in epichlorohydrin (ECO) and fluoroelastomer (FKM) compounds, and is one of the few antioxidants that can survive the processing temperatures used with the latter. It is produced in the United States as Halphos® (Halstab) and addiPhos® (Addenda) and imported as Naftovin® T90 (Chemson) and Pebefos® (Baerlocher). As with normal lead sulfate, normal lead phosphite, $PbHPO_3$, has no value as a heat stabilizer, but has been suggested as a secondary stabilizer for UV light protection, where it is more active than the formally equivalent $CaHPO_3$.[11]

The reaction of PbO with *ortho*-phthalic acid (or anhydride plus water) is usually directed towards formation of dibasic lead phthalate, the most broadly useful of lead stabilizers. This is found in textbooks typically as $2PbO \cdot Pb[C_6H_4(CO_2)_2]$. This is also a Pb—OH compound whose proton NMR spectrum indicates equal numbers of —OH and aromatic C—H protons.[9] Barring an unusual excursion from classical structures, there must be four of each. Therefore, the textbook formula is stoichiometrically incorrect (as well as uninformative). A better description is $C_6H_4[\text{CO—O—Pb—OH}][\text{C(OH)(O—Pb—OH)}_2]$. One might then ask why the reaction product is not tribasic lead phthalate, $C_6H_4[\text{C(OH)(O—Pb—OH)}_2]_2$. If isophthalic acid is used instead, it is indeed the product obtained. Possibly steric hindrance limits the *ortho*-phthalate to a dibasic product. The common reaction product with HCl is again the dichloride. Dibasic lead phthalate dichloride is also very much more water-insoluble than $PbCl_2$.[10] Its NMR spectrum suggests $C_6H_4[\text{CO—O—Pb—OH}][\text{C(OH)(O—Pb—Cl)}_2]$, the two —OH groups that were in close enough proximity to generate split-peak fine structure being lost. This suggests that tribasic lead isophthalate should provide increased failure time from ability to react with more HCl. There is evidence of this being the case, and it would likely be reconsidered if there were not pressure to replace lead stabilizers.

Dibasic lead phthalate has the advantage of increased solubility in a variety of polymers; it is the preferred lead stabilizer for use in PVC blends. A further advantage is that it is almost completely unreactive in promoting hydrolysis of ester plasticizers, unlike the sulfate and phosphite stabilizers. Because of this, the latter are usually used in applications with service ratings of 75 °C or lower. Dibasic lead phthalate may be used in products with service ratings of 90 or 105 °C, and, in other polymers, with higher service ratings. It is produced in North America as Halthal® (Halstab), addiThal® (Addenda), and Demostab® P-80 (Demosa), and imported as Naftovin® T80 (Chemson) and Pebetal® (Baerlocher).

If tribasic lead sulfate and dibasic lead phthalate are coprecipitated in a more or less equal molar ratio, the resultant product has a core/shell structure, a sulfate core, and a phthalate shell.[12] The infrared and NMR spectra of the surface of such coprecipitates is identical to that of pure dibasic lead phthalate. Such products can be substituted for dibasic lead phthalate (at somewhat lower cost) in many applications, usually at 5–7 phr. In lead stabilizers, the cost of the stabilizer is primarily a function of that of the acid used in its preparation. Such coprecipitates are produced as Halstab® 30 and 60 and as addiStab® SP6 and SP7. Although a coprecipitate of sulfate and phthalate has low activity in ester hydrolysis, this does not extend to mere physical blends of the two, which show approximately the average catalytic power.[12]

It is possible to direct the reaction so as to yield monobasic lead phthalate: $PbO \cdot Pb(C_6H_4CO_2)_2$ in textbooks, but actually $C_6H_4(CO{-}O{-}Pb{-}OH)_2$. This product is not a very good stabilizer, and, in addition, is difficult to disperse in soft flexible compounds. Its presence in dibasic lead phthalate is undesirable and should be investigated if dispersion problems are encountered.

If maleic acid is substituted for phthalic, the product is tribasic lead maleate, $C_2H_2[C(OH)(O{-}Pb{-}OH)_2]_2$. This stabilizer is off-white or cream colored and has not been used extensively in PVC. Its major use is as the stabilizer for Hypalon® coatings used in water-resistant tank linings and paint for wire coverings, where (for reasons that are not well known) it provides more stable viscosity and longer shelf life that other lead stabilizers. A minor but significant use is as a burn rate control agent in conventional explosives where a uniform rate of reaction travel is essential, as in the compression of underlying nuclear charges. It is produced in North America as Halstab® TLM (formerly TriMal®), addiStab® TLM, and Demostab® P-91.

If the *trans* isomer of maleic acid, fumaric acid, is used instead, the resultant product has been characterized most often as tetrabasic, but sometimes as polybasic, lead fumarate. It is probably a mixture of $C_2H_2[C(OH)(O{-}Pb{-}OH)_2]_2$ and $C_2H_2[C(O{-}Pb{-}OH)_2]_4$, although intermediate products are possible. As with tetrabasic lead sulfate, this stabilizer is off-white or cream-colored and is UV light-sensitive, again yielding black colloidal PbO. Its major use is in low-smoke flame-retardant PVC compounds, where the long failure time provided helps to compensate for instability caused by other additives, particularly zinc compounds and brominated additives. There would be argument for evaluating lower—cost tetrabasic lead sulfate instead, except for the drive to replace lead stabilizers in the application. Highly flame-retardant compounds may use as much as 10 phr lead stabilizer, often a blend of fumarate with sulfate or phthalate. Tetrabasic lead fumarate is produced in North America as Halstab® TLF, addiStab® TLF, and Demostab® P-89.

Normal lead stearate, $Pb(C_{17}H_{35}CO_2)_2$ (abbreviated $PbSt_2$) is principally a lubricant, at times used as an external lubricant with lead stabilizers. Mixtures of $PbSt_2$ and $BaSt_2$ have been used as stabilizers for phonograph records, where stabilizer demand during processing is not great, and in clear lampcord insulation, although they have been largely superseded in the latter application, first by barium/cadmium and now by barium/zinc stabilizers. $Ba/PbSt_2$ stabilizers can be used when there are modest wet electrical requirements, but are not useful for applications requiring long-term wet electrical testing because of the relative water solubility of the reaction product, $PbCl_2$. Lead stearate is produced in North America as HalLub® N (Halstab), addiLube® NLS, and Demostab® P-28 (Demosa), and imported as Listab® 28D (Chemson) and Baerostab® 28F (Baerlocher).

In addition to normal lead stearate, stearic acid forms monobasic, "half" basic, and dibasic lead stearates. The latter is found in textbooks as $2PbO \cdot PbSt_2$, but is more reasonably $C_{17}H_{35}—C(OH)(—O—Pb—OH)_2$; that is, it is an analog of basic maleate and phthalate. It is a combination internal lubricant/stabilizer used both in flexible and rigid compounds, usually at levels of 0.2–0.5 phr, mainly with tribasic lead sulfate or sulfate/phosphite blends. In North America, lead stabilizers are most often used with barium or calcium stearate as associated lubricant, but in other parts of the world, the use of lead stearate prevails, often as a combination of normal and dibasic forms, providing internal and external lubrication. Dibasic lead stearate is sold as HalLub® D (Halstab), addiLube® DBLS (Addenda), Listab 51 (Chemson), Demostab® P-50 (Demosa), and Baerostab® Pb 51 S (Baerlocher).

Lead stabilizers continue in use because of low cost, high effectiveness leading to long failure times and (usually) gradual failure, reasonable color retention in combination with stearates, and, in the case of dibasic lead phosphite, antioxidant function. Nevertheless, they are toxic substances and should be handled with care. They are best metered directly from semibulk containers into the mixing chamber with suitable dispensing equipment by gravity feed. The installation must be monitored per 29CFR1910.25 and 1910.94 to ensure that lead concentrations in air fall below the time-weighted average threshold limit value (TLV-TWA), currently $0.15\ mg/m^2$ and the permissible exposure level (PEL), currently $0.05\ mg/m^2$. Useful procedural recommendations are presented in *Safety in Handling Lead Chemicals* and in *Controlling Lead Exposure in the Workplace.*[13] Dibasic lead phthalate and phosphite are capable of ignition, generating toxic combustion products.[14] Such fires should be approached only by personnel equipped with independent air supplies.

When not used in applications that justify semibulk handling, lead-in-air requirements are usually met through the use of dispersions, such as prills, extruded strands, or pressed tablets. With direct use of lead stabilizer powder, addition is customarily scheduled with the resin, for which the stabilizer has affinity. The dispersed forms include additives to prevent agglomeration, which often in soft compounds detract from ease of dispersion. With many flexible compounds, stabilizer dispersions are added instead just after plasticizer absorption, treating them as though they were lubricants. Another approach is the use of pumpable paste dispersions in plasticizer, metered into the batch with the latter. Although the physical form of lead stabilizer dispersions (usually) overcomes lead-in-air problems, great care must be taken to avoid ingestion by workers or environmental contamination. Lead stabilizers used in rigid PVC are routinely supplied in combination with lubricants, and often pigments, in dispersed forms called "one packs." These may include all ingredients other than resin. Encapsulation protects lead stabilizers from absorption of carbon dioxide from moist air, the reaction leading to hydrous basic lead carbonate. This tendency increases with basic character, and thus is more of a concern with tribasic and tetrabasic products. The hydrous carbonates formed may hinder dispersion in mixing and may form undispersed agglomerates in wire coverings, leading to electrical failure. On the other hand, the encapsulation system may itself be subject to shelf life, undergoing oxidation or side-chain crystallization, again impeding dispersion and offering opportunity for agglomerates. Therefore, the best procedure remains direct metered addition of the pure stabilizer from semibulk containers into the mixing chamber. It should further be considered that there are individuals who are hypersensitive to lead compounds at levels where most people are apparently unaffected.

All things considered, it would be better if the use of lead-based stabilizers were eliminated. Although there has been a gradual decrease over the years, it seems likely that actual elimination will require legislative intervention. Even though lead stabilizers are highly effective and can be handled safely, there is no reason to formulate general purpose articles with toxic substances when these can be replaced with ingredients that are much safer to humans and to the environment. This is the case with lead stabilizers, as will be discussed below under specific applications.

In using lead stabilizers, formulation should minimize migration of lead-containing species to the surface. Even if the application is such that surface lead would have neither cytotoxic nor ecotoxic consequences, its observation is likely to provoke negative reactions to vinyl. The major external lead species is normal lead stearate. Surface migration is minimized by use of paraffin wax or mineral oil in place of stearic acid. For Frye–Horst displacement of labile chloride, use of calcium or barium stearate will minimize lead migration versus dibasic lead stearate.

Lead stabilizers have a strong tendency to adsorb small molecules. On occasion, oxidized products from additives used in resin manufacture may react with tribasic lead sulfate or dibasic lead phthalate to the detriment of color hold. This tends to vary with lot to lot and with grade of resin. It can be overcome by use of calcium or barium stearate-coated stabilizer or, in severe cases, by replacing 5–10 percent of sulfate or phthalate with dibasic lead phosphite.

4.2.2 Organotin Stabilizers

The largest and fastest-growing segment of the PVC industry in North America is the extrusion of rigid PVC products, pipe, siding, window profile, and synthetic lumber.

This expansion would not have occurred without the development of cost-effective, highly efficient organotin (tin) stabilizers. Theoretically, these applications could use lead stabilizers, and do in other parts of the world. They would not, however, have achieved wide customer acceptance in North America. At the present time, lead stabilizers do not offer a cost advantage, because of the higher levels required. In recent years, tin stabilizers have been developed that are low-cost, may be used at low levels, are broadly independent of other details of formulating, and (often) have low odor.

Tin stabilizers are the only organometallics, other than organosilanes used for coating fillers, and titanates and zirconates used for special purposes, that are broadly found in PVC. Those used are of two types: R_2SnX_2, and $RSnX_3$, dialkyl- and monoalkyltins. Trialkyltins have been used as biocides, but trialkyl- and tetraalkyl tins are too generally toxic for widespread use. Trialkyltin oxides are being phased out as fungicides and barnacle control agents by safer equivalents. The problem is not the metal, but the alkyl group. Tri- and tetraalkyltins are strong methylating agents. The reaction product of their cytotoxic action is the corresponding dialkyltin. Neither dialkyl nor monoalkyltins function as methylating agents, nor are they converted in PVC or other polymers to higher alkylated species. Dialkyltins provide long failure time in PVC; monoalkyltins are more active in displacing labile chloride and provide high color retention. Commercial stabilizers are usually mixtures of the two.

Organotins were first prepared by reaction of the appropriate Grignard reagent with tin tetrachloride, available from the reaction of the oxide reductively with chlorine:

$$SnO_2 + C + 2Cl_2 \rightarrow SnCl_4 + CO_2 \tag{21}$$

$$R\text{—}Cl + Mg \rightarrow R\text{—}Mg\text{—}Cl \tag{22}$$

$$SnCl_4 + 4R\text{—}Mg\text{—}Cl \rightarrow R_4Sn + 4MgCl_2 \tag{23}$$

$$SnCl_4 + R_4Sn \rightarrow RSnCl_3 + R_2SnCl_2 \quad \text{etc.} \tag{24}$$

This was followed by disproportionation of R_4Sn and more $SnCl_4$, as in Reaction (24), which can be controlled to yield mixtures of mono- and dialkyltin chlorides. These are recovered by fractional distillation. The availability of n-butyl chloride led to its routine use. Grignard reagents were subsequently replaced by lower-cost aluminum alkyls, routinely available as chemical intermediates.

Dimethyltin dichloride is now produced directly from tin metal[15] as in Reaction (25), and methyltin trichloride from stannous chloride, as in Reaction (26), both with HCl or other acidic catalyst:

$$Sn + 2CH_3Cl \rightarrow (CH_3)_2SnCl_2 \tag{25}$$

$$SnCl_2 + CH_3Cl \rightarrow CH_3SnCl_3 \tag{26}$$

Methanol is also reactive, yielding the oxide (actually a mixture of cyclic low polymers):[16]

$$Sn + 2CH_3OH \rightarrow [\text{—}(CH_3)_2Sn\text{—}O\text{—}]_{3-4} + H_2O \tag{27}$$

Although this variation would yield noncorrosive products, it has not yet been commercialized. Another synthesis that was put into practice consists of addition of tin to an activated double bond:

$$\mathrm{Sn + 2RO{-}CO{-}CH{=}CH_2 + 2HCl \rightarrow (RO{-}CO{-}CH_2CH_2)_2SnCl_2} \tag{28}$$

$$\mathrm{SnCl_2 + HCl + RO{-}CO{-}CH{=}CH_2 \rightarrow RO{-}CO{-}CH_2CH_2{-}SnCl_3} \tag{29}$$

These products, called estertins, although used elsewhere, did not prove popular in the United States, probably because they did not drop in exactly for butyltin or methyltin analogs. Estertins have low water extractability and received FDA sanction. The FDA-grade products made using Reactions (22–24) are n-octyltins. FDA sanction per 21CFR178.2650 has been extended to a number of methyltin stabilizers as well. The shorter chain length in the alkyl group can be compensated for in the other ligands on tin, leading to correspondingly low extractability. Much research has been devoted to synthesis of tins with higher alkyl groups than methyl. As this is an area of considerable secrecy, it is not generally known whether any butyl- or octyltins are produced commercially by direct reactions.

In some parts of the world, tin stabilizers are viewed unfavorably because of confusion that has lumped them collectively with toxic trialkyl and tetraalkyltin products. This is analogous to anathematizing sodium chloride because it has some relation to HCl; that is, it can be made by reacting HCl with NaOH, two hazardous materials! That the reaction is not reversible under conditions that might be encountered does not counter organized hysteria; the heart of the bad approximation is ignorance of entropy. There is no question that this attitude has inhibited production of useful goods in these areas.

The initial groups used to displace chloride from the SnCl intermediates were carboxylates, such as lauric acid:

$$\mathrm{R_2SnCl_2 + 2C_{11}H_{23}COOH \rightarrow R_2Sn(OCOC_{11}H_{23})_2 + 2HCl} \tag{30}$$

$$\mathrm{R_2SnO + 2C_{11}H_{23}COOH \rightarrow R_2Sn(OCOC_{11}H_{23})_2 + H_2O} \tag{31}$$

The product, in the case of R = butyl, dibutyltin dilaurate (DBTDL), can also be made from the oxide, as in Reaction (31). DBTDL is a stabilizer of only modest effectiveness and is now rarely used in PVC. It is, however, a strong esterification/hydrolysis catalyst, and finds much use in preparation of polyesters, crosslinking of polyurethanes, and in hydrolysis of silanes (previously grafted to polyolefins) to provide siloxane crosslinks. Much more effective stabilizers result from reaction with maleic acid:

$$\begin{gathered}\mathrm{R_2SnO + CH(COOH){=}CH(COOH) \rightarrow} \\ \mathrm{[{-}R_2Sn{-}OCOCH{=}CHCO{-}O{-}]_{\mathit{n}}}\end{gathered} \tag{32}$$

The products, dialkyltin maleates, are low-polymeric solids that have some use in PVC, but are poorly lubricating. They are excellent stabilizers for halogenated flame retardants and are often incorporated by the supplier. More widely used products are generated by reaction both with maleic and with lauric acids, or other lubricating acids, yielding clear, odorless liquids. These are used in light-resistant siding topcoats, in certain flooring applications, and, in general, wherever maximum clarity, high effectiveness, and low odor and volatility are important. It is not entirely certain why the maleate linkage improves effectiveness as compared with to other carboxylates. It seems likely that it facilitates isomerization of *trans–trans* conjugated unsaturation in PVC to *cis–trans* groups, shifting light absorption to lower wavelengths out of the visible range, improving color retention. It is also possible that Diels–Alder addition to double bonds may occur; this requires a *cis* configuration. Or it may be that the group simply facilitates complex formation of the stabilizer with developing degradation sites.

The commercial products in this area often use acids other than lauric, or use blends. Those with an odd number of carbon atoms yield esters that are more resistant to hydrolysis than those with even numbers (a factor also in plasticizer selection). If hydrolysis occurs during processing, there may be volatilization of irritating maleic anhydride fumes. Modern tin carboxylate stabilizers have overcome this problem. In suppliers' literature, they are often designated as "sulfur-free," rather than as organotin carboxylates.

Most tin stabilizers are, however, not sulfur-free. The first commercial tin mercaptide was developed a half century ago by Weinberg, by reacting tin chlorides with thioglycolate esters, such as isooctyl thioglycolate:[17]

$$R_2SnCl_2 + 2HS\text{—}CH_2CO_2C_8H_{17} \rightarrow R_2Sn(S\text{—}CH_2CO_2C_8H_{17})_2 \qquad (33)$$

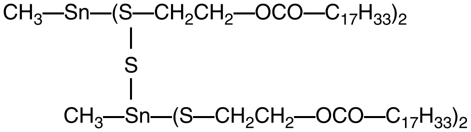
Although this type of stabilizer proved extremely effective in a variety of PVC compounds, its use was restricted by odor considerations. This is a function of traces of isooctyl thioglycolate (IOTG), which, in recent versions of such stabilizers, are removed under vacuum. These are referred to as "low-odor" tin mercaptides. Thioglycolic acid (TGA) also reacts with chloride or oxide intermediates to form low-melting solid low polymers, which have limited use, however, as it is more convenient to meter the esters (which are mobile liquids) into the mixing chamber. Similarly, β-mercaptopropionic acid reacts to form a solid low polymer that is an excellent stabilizer and is sold commercially. It provides comparable failure time to lead stabilizers and much better color retention, and is odorless. Recently, liquid mercaptopropionate esters have been commercialized. These tend to have lower odor and, in some cases, greater effectiveness than the IOTG analogs. Mercaptide ligands are better nucleophiles than carboxylate anions and it is thought generally that this leads to greater effectiveness in stabilization through improved ability to displace labile chloride. As mentioned, the typical end product of this reaction in actual compounds is calcium chloride.

To provide greater lubrication, and thus mobility as a stabilizer, tin intermediates are also reacted with mercaptoethyl oleates, based on inexpensive oleic acid:

$$R_2SnCl_2 + 2HSC_2H_4\text{—}OCOC_{17}H_{33} \rightarrow R_2Sn(SC_2H_4OCOC_{17}H_{33})_2 \qquad (34)$$

Because the ester group faces in the opposite direction from that in IOTG, these products have received the trivial name "reverse esters." Initially, the odor of such species was very noticeable. In recent years, elimination of residual starting materials has again led to relatively low-odor products.

In actual practice, tin stabilizers are often quite complex. There are products on the market that are both carboxylates and mercaptides, made by reaction of dialkyltin oxides with esters in the presence of a tin mercaptide. If a stearate ester is used, the product has increased lubricating value; if a phthalate ester is used, it does not, but may be more useful in phthalate-plasticized flexible PVC applications. Blends of different carboxylates and mercaptides may be used. Some reverse esters are claimed to have —S— bridges between two tin atoms, as in thiobis[monomethyltin-bis(2-mercaptoethyloleate)]:



$$\begin{array}{l} CH_3{-}Sn{-}(S{-}CH_2CH_2{-}OCO{-}C_{17}H_{33})_2 \\ \qquad\quad | \\ \qquad\quad S \\ \qquad\quad | \\ \qquad CH_3{-}Sn{-}(S{-}CH_2CH_2{-}OCO{-}C_{17}H_{33})_2 \end{array}$$

It should be noted that such bridged structures are not universally accepted as realistic depictions. In any event, such boosted-sulfur tin stabilizers, referred to as internally buffered, are able to dispose of HCl by reaction to form volatile hydrogen sulfide as well as by transfer to calcium stearate or another HCl receptor.

Typical butyltin IOTG-type stabilizers have a tin content of about 18 percent and a specific gravity (SpG) of about 1.12–1.13. Methyltin IOTG stabilizers have about 19 percent tin and SpG of about 1.18. Butyltin reverse esters have a tin content in the range of 6–9 percent and SpG of 0.98–1.02; methyltin reverse esters have a tin content of 8–10 percent and SpG of 0.98–1.02. In some products, tin content is increased by addition of alkyltin oxides or sulfides; these stabilizers may have a tin content in the range of 20–25 percent. Octyltin stabilizers have a tin content of 15–16 percent and SpG of 1.08–1.10. All of the above may contain minor amounts of antioxidants, generally to protect the stabilizer itself. They may include additives designed to inhibit partial hydrolysis of the stabilizer, which leads to formation of solid products that interfere with metering into mixing equipment. One that is effective is diphenyl phosphite. Nevertheless, tin stabilizers should be protected from contact with moist air; all air used to drive metering systems should be filtered and dried. Once absorbed into the polymer, the stabilizer retains effectiveness indefinitely.

Although it has been known for some 30 years that active acid absorbers such as zeolite and hydrotalcite have stabilizer value in PVC,[18] data on their use in combination with tin stabilizers has appeared only recently.[19] In general, use of about 1 phr of hydrotalcite or type A hydrous zeolite can provide two advantages: use of tin stabilizer can be cut by up to half, and the type of tin (i.e., the ratio of mono-alkyl to dialkyl), can be adjusted to favor best color retention, the acid absorber taking care of the HCl absorption function. In the case of tin carboxylates or IOTG mercaptides, this can result in overall improved effectiveness plus lower materials cost. A further advantage lies in improved resistance to UV light simply from using a lower level of tin mercaptide. The zeolites and hydrotalcites used are typically surface-coated. A coating of zinc carboxylate is effective with tin IOTG stabilizers, but less so with tin carboxylates and reverse esters. In these cases, special surface coatings have been developed that enable use of zeolites and hydrotalcites with advantage. The mode of failure using this type of acid absorber tends to be gradual rather than abrupt—a practical advantage in production. Having the product discolor, if there is an excursion from desired process conditions, is better than having the compound burn or smoke. Failure behavior with organotin/acid absorber systems is, therefore, similar to that found with lead stabilizers. Interestingly, the NMR spectra of zeolites and hydrotalcites that are useful show chemical shifts and fine structure in the —OH peaks almost identical to those found in lead stabilizers. It is possible that the complex of the degrading site with the tin/acid absorber system is quite similar to that with a lead stabilizer, suggesting that use of lead stabilizers in rigid PVC could be eliminated by use of such combinations. Further uses of these acid absorbers will be discussed as components of mixed metal stabilizers for flexible PVC.

At about the same time as the reactions of tin intermediates with IOTG were noted, Weinberg developed the same procedure for antimony, synthesizing $Sb(IOTG)_3$. This stabilizer is much like the corresponding $RSn(IOTG)_3$ tins; that is, it is fast-acting and yields good color retention. In combination with hydrotalcite or zeolite, both good color retention and failure time can be achieved. In addition, antimony metal is usually less expensive than tin. $Sb(IOTG)_3$ is often made by reaction of antimony oxide, Sb_2O_3, with either IOTG or the precursors, isooctyl (or 2-ethylhexyl) alcohol, and TGA. Isooctyl and 2-ethylhexyl thioglycolates, often taken together as “IOTG,” have different (although less than ingratiating) odors. Thus, the experienced formulator can often tell which has been used in a particular stabilizer. No differences in performance have been reported; usage will depend on relative economics. Methyltin reverse esters are now priced so that their use instead of antimony offers little or no cost advantage. Antimony-based reverse esters can be prepared, but have not been commercialized. Their odor is truly formidable. Antimony carboxylates are odorless, but have poor heat stability and have not been used in stabilizers.

$Sb(IOTG)_3$ has been used in pipe, but mainly in rigid PVC conduit for insulated wire. Although the UV light resistance of tin mercaptides is not very good, that of antimony analogs is worse. Adding to these factors is the perception of antimony toxicity. Although $Sb(IOTG)_3$ is of low enough toxicity and extractability to have been approved by the National Sanitation Foundation (NSF) for use in water delivery pipe, attempts to have it removed from the EPA list of toxic substances “antimony compounds” category failed. The product of its use in stabilization of pipe is calcium chloride. Nevertheless, EPA could not be convinced that unreported reactions might somehow generate toxic products. The combination of the above factors has largely eliminated the use of antimony stabilizers.

4.2.3 Organotin Stabilizer Usage

Potable water pipe, also referred to as pressure pipe, uses a relatively standard recipe, having NSF approval, in the United States. It is almost always produced using multiscrew extrusion. If a single-screw extruder is used, the stabilizer level should be raised from that shown below to the range of 0.8–1.5 phr, and 2–2.5 phr of a processing aid added.

PRESSURE PIPE

PVC (K-65)	100
$CaCO_3$ (0.8 μm)	2–4
TiO_2 (rutile)	1–2
$CaSt_2$	0.4–0.8
Paraffin wax (165 °F mp)	0.8–1.0
Oxidized PE wax	0.1–0.2
Stabilizer	0.4

Recommended stabilizers include Thermolite® (Atofina) 140 and 176; Mark® (Chemtura) 1939 and 1996. Advastab® (Rohm & Haas) TM-694 and 697; Interstab® (Akcros) T-5277 and Reatinor® RT-6611 and 6612 (Reagens). Some of the reverse ester stabilizers for pipe applications have boosted tin levels and may be used (in favorable circumstances) at 0.3 or 0.35 phr instead of 0.4. In the above recipe, $CaCO_3$ and TiO_2 provide the necessary opacity, the latter adding UV light resistance. The levels are held low to maximize burst resistance and impact strength. The remaining ingredients comprise the lubricant package. The level of $CaSt_2$ is adjusted to provide the optimum fusion speed during extrusion and to provide internal lubrication; the level of paraffin wax is adjusted to provide external lubrication. For convenience in adding to the mixer, flaked paraffin wax, such as MarkPet® (Chemtura) or Sunolite® 160 (Sun Oil) may be replaced by refined paraffin oil, such as MarkLube® PW-10. The use of low levels of oxidized PE wax improves printability and tends to add combination action to the lubricant system.

In some parts of the world, the above formulation would be run with a stabilizer composed of 0.5–1.0 phr of stearate-coated tribasic lead sulfate and 0.2–0.3 phr dibasic lead stearate, typically with 1–2 phr of an ester lubricant and reduced paraffin wax. For a gray product, a blend of TiO_2 and fine-particle carbon black would be used to provide UV light protection. Although such pipe has been in service for many years without confirmed ill effects, the use of lead stabilizers cannot be recommended, since it is unnecessary, of no significant cost advantage, and detracts from popular acceptance. If (actually when) it becomes necessary to convert from use of lead stabilizers in rigid PVC, it is simpler to convert to a calcium/zinc system than to organotin. The lubrication values of lead and Ca/Zn stabilized compounds are similar and neither requires protecting steel surfaces from sulfur corrosion from tin mercaptides. In addition, there is no concern with lead–sulfur staining. Materials cost will increase from the cost and the much increased stabilizer level needed (3–4 hr), and output may also suffer. An intermediate step is to convert pressure pipe only, as is being done in parts of Europe, with a lead one pack being replaced by a Ca/Zn one pack, such as Reapak® B-TU/1020 and 1062 (Reagens) or Naftomix® 1520 and 1524 (Chemson).

In North America, CPVC pipe uses stabilizers high in tin content, such as Akcrostab® T-4905, Mark® 1900, Advastab® TM-161, Thermolite® T-31, or functional equivalents. Lead stabilizers are used elsewhere.

PVC pipe used for low-pressure applications for drain, waste and vent purposes (DWV) is more highly extended, but similar:

DWV PIPE

PVC (K-65)	100
Impact modifier	2–3
$CaCO_3$ (0.8–1.0 μm)	10–40
TiO_2	0.5–1.0
$CaSt_2$	0.6–0.8
Paraffin wax (165 °F mp)	1.2–1.5
Oxidized PE wax	0.1–0.2
Stabilizer	0.3–0.5

The most common practice is to use the same stabilizer throughout the plant. (Note that any blending of different tin stabilizers, even those thought equivalent, should be done only after thorough small-scale evaluation so as to preclude unexpected effects from minor additives.) With the higher filler loading used in this application, it is necessary to add an impact modifier. The same is true with electrical conduit, where the above recipe also applies, except that TiO_2 is often reduced or eliminated, or blended with carbon black to generate a gray product. Processing aids are sometimes added with DWV and conduit extrusions, particularly if single-screw extruders are used. In the latter case, stabilizers are used at a 0.8–1.5 phr level. In areas where lead stabilizers have been used, conversion has begun with Ca/Zn one packs, such as Reapak® G-Tu/1059 or Naftomix® 2300, at 2–3 phr.

Except in cases where the outer layer is acrylic, for example, Acryligard® (Rohm & Haas) or PVDF (Kynar®), vinyl siding is extruded in dual layers, mainly an inner layer, "substrate," and the outer weatherable layer, "capstock." (The terms come from siding jargon that predates the appearance of PVC.) The bulk of the product is, of course, substrate, which uses reverse ester tin stabilizers:

SIDING SUBSTRATE

PVC (K-65)	100
Impact modifier	3–5
$CaCO_3$	7–15
TiO_2	0–1
$CaSt_2$	1–1.2
165 wax	1–1.3
Oxidized PE wax	0.1–0.2
Stabilizer	0.8–1.2

Recommended reverse ester tin stabilizers include Thermolite® 140, 172 butyltins and 174 methyltin; Mark® 1367 butyltin and 1939, 1971, 2903 methyltins; Advastab® TM-286SP; and Interstab® T-5201 and 5286. Substrate recipes may also include 0.15–0.25 phr of a lubricating processing aid. Addition of zeolite or hydrotalcite at a level of 0.5–1.0 phr will enable use of the low end of the above recommended usage and will provide for gradual rather than abrupt failure in case of factory misadventure. A suitable costabilizer for this purpose is Halstab® 1214 coated zeolite.

Even though filler extension is low, impact modifiers are required because of processing: extrusion of a flat sheet, embossing of a pattern simulating wood, and thermoforming to the complex shape of the siding, as well as for protection from impact during installation and in service. Vinyl siding has as yet made only slight penetration of the European market. It is anticipated that products will use the Ca/Zn one packs that are replacing lead stabilizers in window profile.

Capstock stabilizers tend to be based on tin IOTG. A typical recipe comprises the following:

SIDING CAPSTOCK

PVC (K-65 to 68)	100
Impact modifier	4–6
TiO_2	8–10
$CaSt_2$	1–1.5
165 wax	1–1.5
Processing aid	0.2–1.0
Tin IOTG stabilizer	0.8–1.2

Recommended stabilizers include Thermolite® 161, 172, 174, 340, and 380; Mark® 1367, 1900, and 2284A; Advastab® TM-181 and TM-186; Interstab® T-5003 and 5262; Reatinor® 414 (Reagens); PlastiStab® 2820 (Halstab); Baerostab® M 25S (Baerlocher); and Therm-Chek® 840 (Ferro). There is also now some use of reverse ester tins with relatively high tin levels, such as Mark® 1971, Advastab® TM-182 and TM-697, and Interstab® T-5278, recommended at 1.4–1.75 phr. Improved UV light resistance can be gained by use instead of a combination mercaptide/carboxylate stabilizer such as Mark® T-634, or 2270F, recommended at 2–3 phr, or of a high efficiency tin carboxylate, such as PlastiStab® 2808 (Halstab), Therm-Chek® 835, Reatinor® 460, or Interstab® T-876 and T-878. These options should be considered for siding applications in Southern locations, as well as the use of acrylic topcoats. Improved UV light resistance with tin mercaptide stabilizers also results from addition of about 1.0 phr of a costabilizer such as Halstab® 1214 and reduction of stabilizer level. Ca/Zn stabilizers that might be considered include Baerostab® B 634 and MC 9041 FP/1 and ThermChek® RC 437P.

Impact modifiers are again used despite the low filler loading because of processing and service requirements. In nonwhite versions, pigment is used in both layers, not merely to permit a description of being uniformly colored, but because the capstock would be hard pressed to carry sufficient pigment. In some cases, sufficient titanium dioxide is added to the substrate in white siding as to make it difficult to distinguish the components visually.

Window and picture frame profile extrusions use compounds similar to siding capstock recipes but typically are based on slightly higher molecular-weight resin, compensating for an increased additive package designed for maximum extrusion line speed.

PROFILE EXTRUSION

PVC (K-67)	100
Impact modifier	5–6
Processing aid	0.7–1.0
Lubricating processing aid	0–0.2
$CaCO_3$ (0.8 μm)	0–5
TiO_2 (or blend with pigment)	8–10
$CaSt_2$	0.8–1.2
165 wax	0.8–1.2
Stabilizer	1–1.5

Recommended stabilizers include Thermolite® 161 and 380; Mark® T-634, 2284A, 1900 and 1996; Advastab® TM-181 and TM-186; Akcrostab® T-5003 and T-7020; Reatinor® 403 and 404; and Therm-Chek® 840. Again, it may be advantageous to add 1 phr of a zeolite acid absorber, such as Halstab® 1214 while reducing the stabilizer to 1 phr. In Europe, lead and lead/cadmium one packs have started to be replaced by Ca/Zn stabilizers, such as Naftomix® 6300 and 6500, or Baerostab® B 634 and MC 9041 FP/1, at 2–3 phr.

Food-grade blow-molded bottles use ingredients FDA sanctioned per 21CFR 178.2650 at permitted levels, with low-odor octyl or methyltins:

FOOD GRADE BOTTLE

PVC (K-57)	100
MBS impact modifier	12–15
Processing aid	1.5–2.0
Lubricating processing aid	0.5–1.0
Internal lubricant	1.5–2.0
External lubricant	0.1–0.2
Stabilizer	1.5–2.0

Recommended stabilizers include Thermolite® methyltin 190, and octyltins 890 and 890S; Mark® OTM octyltin or methyltin 1995; Akcrostab® methyltin T-7021 and octyltin T-883; Reatinor® octyltins 804 and 807; and PlastiStab® 2807. Up to

2.0 percent by weight of stabilizer may be used per the above FDA sanction. Food-grade rigid PVC sheet uses the same stabilizers and is similar:

FOOD GRADE SHEET

PVC (K-60)	100
Impact modifier	6–12
Processing aid	1.5–2.0
Lubricating processing aid	0.7–1.0
Internal lubricant	1.2–1.5
Stabilizer	1.2–1.5

In both cases, toners may be added to provide a bluish tint. General purpose (non-food-grade) clear sheet traditionally used 2.0–2.5 phr of a carboxylate stabilizer, such as PlastiStab® 2808, Therm-Chek® 835, Reatinor® 460 or 480, or Interstab® T-876 or T-878; or a carboxylate/mercaptide, such as Mark® T-634 or 2270F, or Akcrostab® T-5507A. With the advent of low-odor tin mercaptides, much of this has been converted from the more expensive carboxylates. For clear extruded sheet, the following is typical:

CLEAR EXTRUDED SHEET

PVC (K-60)	100
Impact modifier	5–10
Processing aid	1–2
Lubricating processing aid	0.4–1.0
Oxidized PE wax	0–0.2
Internal lubricant	0.5–1.0
Stabilizer	0.8–1.7

Suitable stabilizers include Thermolite® 108, Mark® 2270F, Akcrostab® T-5063, Advastab® TM-181 and TM-186, and functional equivalents as described above. Clear calendered sheet is similar, except for higher levels of internal lubricant (1.2–1.5 phr), processing aid (1.5–2.0 phr), lubricating processing aid (0.7–1.0 phr), and usually the addition of 0.1–0.5 phr of an external lubricant. In Europe, Ca/Zn one packs, such as Naftomix® 7205, are also used at 2–3 phr. Corrugated clear roofing has tended to retain the use of carboxylate stabilizers, and generally includes a UV light absorber and high levels of acrylic impact modifier:

CORRUGATED CLEAR ROOFING

PVC (K-58 to 60)	100
Impact modifier	6–15
Processing aid	0.5–1.0

Lubricating processing aid	1.0–1.5
Internal lubricant	0.8–1.0
External lubricant	0.2–0.3
UV light absorber	0.3
Stabilizer	2–3

Clear rigid profiles for outdoor use are very similar. For general purpose rather than outdoor use, pigmented opaque sheet is similar except that low-odor tin IOTG stabilizers are used. The levels of impact modifier, processing aids, and lubricants vary with the extent of filler and pigment usage.

The most common injection-molded items made from rigid PVC are pipe fittings. Butyltin and methyltin IOTG stabilizers are used.

PIPE FITTINGS

PVC (K-55 to 58)	100
Impact modifier	0–5
Processing aid	0–1.5
Lubricating processing aid	0–0.5
$CaSt_2$	1–1.5
165 wax	1–1.5
TiO_2	1–3
Stabilizer	1.5–2.0

Stabilizers specifically recommended include Thermolite® 31S, 108, and 161; Mark® 1900; Advastab® TM-181 and TM-2831M, Akcrostab® T-7020; and others noted above for use in profile or capstock formulations. Impact modifier level will increase as the size of the fitting becomes greater. Weatherable fittings, such as for pipe used outside in decorative or garden applications, have low levels of calcium carbonate added, requiring use of an impact modifier, typically 2–3 phr.

Injection-molded electrical boxes use blends of titanium dioxide and carbon black for exterior (gray) products. Interior electrical boxes are often colored blue. All are deep-draw complex moldings, requiring processing aids and lubricants at the upper end of the above range. In addition, impact modifiers are used at a 2–5 phr level. Use of a large additive package to facilitate injection molding can sometimes prejudice heat distortion under load characteristics. An approach that provides some compensation for this is the use of solid tin stabilizers. A particularly effective choice is dibutyltin mercaptopropionate (Mark® 2255, Akcrostab® T-186), used at a 1–2 phr level. Alternatively, it can be used at 1 phr with 1 phr of a treated zeolite booster, such as Halstab® 1214. In Europe, Ca/Zn one packs, such as Naftomix® 1911, are also used, at about 3 phr.

Tin powders also find use in injection-molded CPVC, such as for electrical boxes, to maximize resistance to heat distortion. Other tin stabilizers used in molded CPVC include Thermolite® 30S, Advastab® TM-161, Mark® 1900, and Akcrostab®

T-4905. An interesting CPVC costabilizer is the Ferro UV light Na/Ba/organophosphate stabilizer UV-Chek® AM-595.

One of the most rapidly expanding areas of PVC technology is that of rigid foam products, leading to "foam core" pipe, siding substrate, sheet, profile, and wood composites (plastic lumber). Comparisons between formulations for solid and foamed products are illustrative:[20]

DWV PIPE AND FOAM CORE AND SKIN

	DWV Pipe	Foam Core and Skin	
PVC (K-65)	100	100	100
Impact modifier	2	—	—
Processing aid	—	2–4	0.2–1.0
$CaSt_2$	0.6–0.8	0.6–0.8	0.6–0.8
165 wax	1.2–1.5	0.8–1.0	1.0–1.2
Oxidized PE wax	0.1–0.2	—	—
$CaCO_3$	10–30	5–10	3–5
TiO_2	0.5–1.0	0.5–1.5	1.0–1.5
Stabilizer	0.3–0.5	0.4–0.6	0.3–0.4
Blowing agent	—	0.3–0.5	—

What does not appear in the formulation is the effect of foaming, a decrease in overall density of almost a factor of three. In comparison, the increase in additive usage is trivial in cost. Although requiring special purpose extrusion equipment and careful control, foam core pipe is much more convenient to install in the field than solid pipe and has gained acceptance in larger sizes. In the United States, the blowing agent is typically azodicarbonamide, which is activated in a useful temperature range by calcium stearate. Foam core pipe is also gaining acceptance in Europe, using either lead or Ca/Zn one packs, such as Naftomix® 1805 and Baerostab® B 1035. The comparison of solid and foam extruded sheet is similarly instructive:

SOLID AND FOAM SHEET

	Solid Sheet	Foam Sheet
PVC (100 phr)	K-67	K-60
Impact modifier	5–10	2–4
Processing aid	1.5–2.0	4–6
Lubricating processing aid	0.1–0.4	—
$CaSt_2$	0.6–1.0	0.3–0.5
165 wax	—	0.6–1.0
$CaCO_3$	0–5	7–10
TiO_2	0–1	1–3
Stabilizer	0.8–1.7	0.7–0.8
Blowing agent	—	0.3–0.5

The resultant products are very useful. The effects of foam density on properties have been reported by Patterson.[21] Thermal conductivity is reduced greatly, stiffness is increased, and the product can be cut, sawed, or nailed much like another cellular polymer, wood. The logical conclusion is to combine the cellulosic compound, wood, with PVC to generate plastic lumber. Typically azodicarbonamide (and often foam structure control agents) are added, but Matuana has reported that, without drying, moisture in the wood fiber can be used as the blowing agent.[22] Typically, however, the wood fiber is dried thoroughly and often coated so as to generate a hydrophobic surface. At first, coatings of $CaSt_2$ and ethylene bis-stearamide (EBS) were used. More recently, proprietary coatings such as Glycolube® WP-2000 (Lonza), Mark® W15, TPW® 012 and 251 (Struktol), and Safoam® WSD and WLB (Reedy) have been used. At this point, a scavenging agent may be added to the wood fiber to sequester tannins, which are generated by various trees as parasite controls. These are phenolic compounds that are powerful chromophores; their solubility in water leads to migration to the surface, where a variety of light-colored articles in contact with the PVC/wood composite may be noticeably stained. One that has been reported is Carboquat® (Lonza).

PVC WOOD COMPOSITE

PVC (K-65)	100
Wood fiber	10–80 but typically 50–60
Processing aid	2–6
Lubricating processing aid	0–1
$CaSt_2$	0.6–1.2
165 wax	1–1.2
Oxidized PE wax	0–0.2
Stabilizer	1–2
Azodicarbonamide	0.4–0.6

Despite encapsulation by PVC, compounds such as the above should contain a biocide if used as plastic lumber outdoors. Those reported effective include thiazolyl benzimidazole (Irgaguard® F3000; Ciba), dichlorooctylisothiazolone (Vinyzene® SB27 (Rohm & Haas) and Micro-Chek® 11 (Ferro), and zinc borate (Borogard® ZB; US Borax). Wood fiber composites are discussed in greater detail in Chapter 17.

4.2.4 Tin Stabilizers in Flexible PVC Compounds

The major use of tin stabilizers in flexible PVC is in flooring topcoats and foamed plastisols produced in Europe. Carboxylates such as those described above for best weatherability in profile and siding capstocks are used at 1–2 phr. There is no question that this approach provides exceptionally good color retention during processing and service. Cost considerations work against analogous use in North America, where such applications are served by Ba/Zn, Ca/Zn and Zn-based stabilizers that are actually mainly epoxidized oil and phosphites. Flooring applications where unusually severe processing conditions are likely, such as in vinyl chips used in plastisol coatings, often use tin maleate esters.

There are a number of minor uses of tin stabilizer in flexible PVC compounding. These, as with flooring components, typically date from times when the only suitably effective mixed metal stabilizers were based on cadmium. A common characteristic of these diverse uses is poorly controlled processing conditions. For example, the coating of wire lobster traps with plastisol can involve fusion in homemade ovens of variable and uncertain temperature. The same situation may occur in cottage industry manufacture of doll parts from plastisol. In such cases, the cost of the stabilizer may be irrelevant, and a tin maleate ester is a good choice. It is often not worthwhile for stabilizer suppliers to pursue such accounts with high-efficiency Ca/Zn liquids.

FDA-sanctioned octyltin and methyltin stabilizers are also used in food packaging film and sheet, where relatively low levels of plasticizer are added to add flexibility. With 20–40 phr plasticizer, 1.5–2.0 phr such as Mark® OTM, Thermolite® 890, or others listed above in connection with food-grade bottles can provide brilliant clarity.

Flame-retardant flexible PVC compounds that use brominated plasticizers or other additives are likely to contain a tin maleate powder, used as stabilizer in the flame retardant. Available products include Mark® 2100A and Reatinor® 1044.

4.2.5 Design of Commercial Tin Stabilizers

As mentioned above, the intimate details of composition of stabilizers other than those based on lead are not generally available. Suppliers will routinely provide data such as the type of alkyl group, the tin content, whether or not the ligands contain sulfur, and observable properties, including refractive index, color, SpG, flash point, and viscosity. Suggested uses often contain starting point recipes (such as those given above). For significant uses, supplier technical service will extend to consultation regarding running specific products. Excellent reference guides include the AtoFina and Rohm & Haas publications, *Plastics Additives*.

4.3 NONMETALLIC STABILIZERS

It has been known at least since 1952 that esters of β-aminocrotonic acid, $CH_3—C(NH_2)=CH—CO_2R$, have a stabilizing effect in PVC. Possibly, labile chloride is transferred to the amine group or to calcium stearate. Evolved HCl may also be transferred to an acid absorber by such additives. In the preferred embodiment, thiodiethylene glycol bis(β-aminocrotonate), $[CH_3—C(NH_2)=CH—CO_2—CH_2CH_2]_2S$, sulfur displacement of labile chloride is likely. In combination with calcium stearate, this stabilizer is effective in relatively low demand processing, as in multiscrew pipe extrusion. It is sold in Europe as a one pack including lubricants as Mark® A70.

In the 1980s, Ciba developed a new class of nonmetallic stabilizers based on the carbon–nitrogen six-membered ring heterocycle 1,3-dimethyl-4-aminouracil. In combination with calcium stearate for fusion control and often with zeolite as acid absorber, this stabilizer is effective in PVC pipe and has a number of approvals, particularly in nonwhite applications. The commercial product, now called OBS 100 (Chemtura), is reported to contain 2.2–3.0 percent nitrogen and 3.5–6.4 percent calcium. In parts of Europe, the diethyl and di-n-butyl analogs are used in clear rigid sheet, not imparting haze as does the dimethyl additive. The butyl groups may also reduce water extractability; dimethyl aminouracil is very water soluble. It is possible that the primary effect of nonmetallic stabilizers is merely to reverse the initial step of HCl-catalyzed HCl elimination, per Reactions (15) and (16) above.

Recently, Starnes and Zaikov have reported that thiol esters such as 2-ethylhexyl 3-mercaptobenzoate function as efficient stabilizers both by displacement of labile chloride and addition to polyene sequences.[23] In this case, good performance was noted with high-shear dynamic stability testing, using 3 phr of thiol plasticizer/stabilizer. Although it is difficult to visualize such a system being competitive with low-cost tin stabilizers used at levels as low as 0.3 phr, it will, nevertheless, be of interest to follow commercialization of this approach.

4.4 MIXED METAL STABILIZERS

Although not usually characterized this way, it can be seen from the discussion above that there are basically two types of PVC stabilizer. There are stabilizers for use when the compound is subject either to high shear for extended time periods, as in single-screw extrusion and calendering, or to very high shear rates for a briefer period, as in injection molding. Such compounds are best served by, for example, 1 phr or higher of a tin stabilizer with high tin content, or several phr of a lead stabilizer. The second class of compounds is either subject to high shear only very briefly, as in multiscrew extrusion, or does not develop high shear at all because the compound is very soft at processing temperatures. Thus, remarkably low levels of reverse ester tin stabilizers having single-digit tin content can be used to produce PVC pipe or siding substrate. Rheometer dynamic stability curves on such compounds are astounding when first seen. Almost immediately after completion of fusion, where one might expect a plateau, there is merely a valley before crosslinking and degradation begin. With modern equipment, it is all the stabilization that is needed. The manufactured pipe or substrate will have up to 90 percent of its original stabilizer content unused.

Until recently, the only mixed metal stabilizers that fit comfortably in the first class above were those based on barium and cadmium compounds. Barium and cadmium cations are good traveling companions; they are almost the same size. Carboxylate groups can bridge Ba(II) and Cd(II) readily. A stabilizer based on a blend of barium and cadmium stearate is reasonably represented by the notation St-Ba-$(St)_2$-Cd-St, that is, a complex. High barium content led to long failure time; high cadmium, to best color retention, clarity and sparkle. Liquid mixed metal stabilizers for demanding applications were, therefore, either 2 : 1 Ba : Cd (often 10 : 5 weight percent in pure metal analysis); 1 : 2 Ba : Cd (often 5 : 10 weight percent); or a compromise 1 : 1 Ba/Cd, depending on the attributes thought most important. Zeolite or hydrotalcite can be used as the primary acid absorber instead. A blend of about 60 percent zeolite, 30 percent cadmium stearate, with the remainder being barium stearate and antioxidant, yields a stabilizer of comparable effectiveness to dibasic lead phthalate or high-tin mercaptide. Although Ba/Cd/zeolite powders as well as Ba/Cd and Ba/Cd/Zn liquids are still sold, they should be replaced. Soluble cadmium compounds are ecotoxic and carcinogenic and should not be used in plastics additives. Their usage in PVC adds to pressure to use competitive plastics. It should be noted that humans have been exposed to the levels of cadmium naturally occurring in zinc compounds for millennia and that such traces are apparently innocuous.

The relation of efficient HCl absorption, leading to long failure time, and replacement of labile chloride with poor leaving groups, leading to improved color hold, has always been complex in the case of mixed metal stabilizers. In a stabilizer composed mainly of organophosphite and epoxidized soybean oil (ESO) with small amounts of a zinc carboxylate, such as in medical tubing, it is likely that HCl absorption is directed by zinc to ESO, and labile chloride displacement, by zinc-catalyzed Arbusov reaction of the phosphite (Section 4.4.2.3). The latter is analogous to Frye–Horst[4] labile chloride replacement by the mixed metal combination and has been explored in experimentation by Michael Fisch and Radu Bacaloglu.[24] That epoxides can, and in some cases apparently do function in labile chloride displacement, was pointed out by Donald Anderson in 1970.[25] Similar experimentation with polyols was described by Iida and co-workers.[26] As with polyols as costabilizers, labile chloride displacement involving epoxides may also lead to complexes with zinc that are less subject to zinc chloride formation. With use of highly efficient HCl absorbers such as zeolite or hydrotalcite, reliance on ESO costabilization is typically reduced or eliminated.

4.4.1 Mixed Metal Powder Stabilizers

Stabilizers in powder form have the advantage of long shelf life and resistance to hydrolysis under ambient conditions. They are convenient to use with filled compounds by addition to the mixer, sometimes preblended, with the filler or pigment. If used in clear compounds, powder stabilizer is added with the resin. A further advantage is low volatility during service and, with proper choice, low extractability. On the other hand, liquid stabilization ingredients, such as epoxidized oils or most organophosphites, must be added separately. In practice, if the above advantages are irrelevant to the application, it is more convenient to use a liquid stabilizer added to the plasticizer.

Powder stabilizers described as lubricating are based on blends of stearates, originally barium and cadmium, or barium, cadmium, and zinc, but now mostly barium or calcium with zinc. Moderately lubricating powders are based on laurates rather than stearates. Minor amounts of calcium carbonate may be added to aid dispersion, or titanium dioxide for color improvement. At one time, Ba/Cd stabilizers contained a minor fraction of BPA as antioxidant; Ca/Zn stabilizers used BHT, or BHT and a thiodipropionate secondary. These have been largely replaced in modern Ba/Zn and Ca/Zn stabilizers with more effective antioxidants (as described above). Powders often contain polyols such as pentaerythritol (PE200®). These function as HCl scavengers during processing through elimination of the elements of water at elevated temperatures and addition of HCl to the double bond that is formed, probably in a concerted reaction with zinc or cadmium catalysis. Such reactions may also lead to displacement of labile chloride from the resin, again with primary metal catalysis. Stabilizers containing PE200 may also include benzoic acid, probably forming pentaerythritol benzoate *in situ*, thus leading to lower water solubility and moisture absorption. It is possible that metal stearate—PE200 blends may form pentaerythritol esters (ester lubricants) during processing. In Ca/Zn pastes, glycerol is sometimes used for the same purposes.

The most important recent ingredients for powder stabilizers are zeolite and hydrotalcite. Type A (containing sodium cations) hydrous zeolite is a complex microporous aluminosilicate able to exchange 18–20 percent of its weight for HCl, liberating water. For it to function efficiently, a tin or mixed metal stabilizer must be able to complex the degrading site and transfer HCl to zeolite. Products on the market include Valfor® 100 (PQ Corp.), EZA® (Albemarle), Advera® 401 (PQ Corp.), and Halstab® 1214. Zeolite-based powders can be used in filled and translucent compounds such as floor mats. Use in truly clear products awaits the availability of submicron grades, that is, particle size too small to scatter light.

Hydrotalcite is a platy form of magnesium aluminum hydroxycarbonate. It exchanges carbonate for chloride, eliminating CO_2 and sequestering HCl. The reaction product appears to have much lower hydrophilic character than that formed by zeolite. Again, an active stabilizer is required to transfer HCl from the degrading site to hydrotalcite. Suitable products are produced by Kisuma (Alcamizer®), Sud-Chemie, and others. There is also an array of "hydrotalcite-like" substances that function similarly, including calcium-based analogs used in powder stabilizers supplied by Baerlocher. It is also possible to use other anions than carbonate, such as phosphite, for improved color retention, or perchorate, to inhibit amine stain (see Section 4.4.1.2). Hydrotalcite-based powder stabilizers are used primarily in filled compounds. In clear compounds, it is possible to use low levels of submicron grades of hydrotalcite (e.g., Kyowa DHT-4A) that are produced for use in clear polyolefin compounds to scavenge Ziegler–Natta polymerization catalyst residues.

4.4.1.1 Wire and Cable

A major area of powder mixed metal use is in replacement of lead stabilizers in wire insulation and jackets. Jackets having minimal wet electrical requirements have the longest history of use. These were at first Ba/Zn powders (or liquids) but with improving technology, are now mostly Ca/Zn/zeolite or Ca/Zn/hydrotalcite blends. Standard test recipes are as follows:

NM-B JACKET COMPOUND

PVC (electrical grade, medium molecular weight)	100
DIDP (electrical grade)	55–60
$CaCO_3$	50
Stearic acid	0.25

Ca/Zn stabilizer	1.8–25
Epoxidized soybean oil (ESO)	0–5

The above formulation is a starting point towards 70 °C rated nonmetallic building wire (NM-B) jackets. Recommended stabilizers include Therm-Chek® RC 488P (Ferro), PlastiStab® 2165 (Halstab), RVP® 102 (Amfine), Mark® 6797 and 6782 (Chemtura), and Baeropan® B 1011 (Baerlocher). The variation in stabilizer level comes from two factors: the lead stabilizer being replaced, tribasic lead sulfate, is a good white pigment. Therefore, it may be useful to add a small amount of titanium dioxide. The basic level of stabilizer needed in most jacket formulations for processing and heat aging tests is in the 1.6–1.8 phr range. If this is diluted with calcium carbonate and a little titanium dioxide, the resultant 4–5 phr then used may end up in about the same material cost area as 4–5 phr of tribasic lead sulfate. In addition, the computerized instructions for ingredient addition to the mixer may be left unchanged. Since these products do not cross-stain, remnants of previously used lead stabilizers may be worked away.

The above-mentioned stabilizers are useful not only for building wire jackets but also in flexible cord and communications wire insulations; that is, in applications not having severe wet electrical testing requirements. The use of ESO or a liquid organophosphite may or may not be useful with a particular stabilizer; the supplier's literature should be consulted. For NM-B insulation, which requires insulation resistance to level off during 6 months in water at 75 °C, Ca/Zn stabilizers must be based on hydrotalcite rather than zeolite. A typical starting point formulation comprises the following:

THWN INSULATION

PVC	100
Calcined clay (electrical grade)	10
Calcium carbonate	5–10
TINTM plasticizer or equivalent	25
UDP plasticizer or equivalent	25
Ca/Zn/hydrotalcite stabilizer	4–7

In practice, 2–5 phr antimony oxide is usually added. Recommended stabilizers include Mark® 6784; Therm-Chek® 7208, RC 215P, and RC 600P; and PlastiStab® BN122 and Baeropan® B 1055. For wet electrical testing at 90 °C, calcined clay should be silane-treated to minimize water pickup, the plasticizer should be all-branched-chain trimellitate, and the formulation should be as simple as possible. Mobile additives should be minimized and as high a molecular weight resin as feasible chosen. The elements that work against water absorption, the cause of decreasing insulation resistance, include not only minimization of hydrophilic ingredients, but also generating as high a low extension modulus as possible. Some suppliers recommend special stabilizers for Underwriters Laboratories (UL) category THWN-2 (90 °C wet electrical testing) such as Therm-Chek® RC 215P and 600P.

In building wire for direct burial (UL Type UF), it is suggested that a water-resistant lead replacement stabilizer be used also in the jacket, whether or not so required by specifications. Similarly, in so-called "double-insulated" cords, both insulation and jacket should be water-resistant.

Before the advent of suitably flame-retardant crosslinked EVA insulation compounds, peroxide and radiation-crosslinked blends of PVC/VA solution copolymers and EVA were used for switchboard wire and related applications. These compounds routinely passed 90°C long-term wet electrical testing and 7-day heat aging at 150 °C. This is an approach that might be reconsidered.

Automotive primary wire, although having minimal wet electrical requirements, must pass severe heat aging and must be of low cost. Compounds in practice are similar to building wire insulation in that low filler loadings and highly nonvolatile plasticizers are used, but with Ca/Zn/zeolite stabilizers. Recommended stabilizers include Mark® 6782, Therm-Chek® RC 440P, Baeropan® MC 8705 KA, and PlastiStab® BL559. Ba/Zn powders, such as Halstab® 1505, are also used. Automotive wire stabilizers are often formulated to be used at 4–6 phr; that is, to drop in for tribasic lead sulfate. As with lead replacement in general, the compound usually must be adjusted to compensate for the Ca/Zn or Ba/Zn stabilizer having greater lubrication value.

Another demanding application is the stabilization of PVC jackets for plenum cables and related low-smoke flame-resistant applications. The underlying problem is the need to stabilize brominated flame retardants as well as the resin, and to counteract the destabilizing activity of various low-smoke additives, such as zinc borate and ammonium octamolybdate (AOM), and that of phosphate plasticizers. The solution is basically the use of a lot of stabilizer—typically 4–6 phr of a Ca/Zn/zeolite such as would be used for automotive wire. Some suppliers offer specific products, such as Mark® 6783, Baeropan® MC 9108 KA, and Therm-Chek® RC204P. The following is a starting-point recipe:

PLENUM CABLE JACKET

PVC	100
ATH	60
FR plasticizer	40
Zinc borate	9
AOM	4.5
Antimony oxide	1
Antioxidant	0.2
Stearic acid	0.2
Stabilizer	4–6

Stabilizers for primary insulation are also suitable for electrical tapes that previously used dibasic lead phosphite.

4.4.1.2 Automotive Interior Components An area where lead stabilizers have been replaced in most parts of the world comprises vinyl compounds used in automotive interiors. Stabilizers must provide good color hold during service and must be low-fogging; that is, they must not emit volatiles that would deposit on windshields at temperatures, in direct sunlight, in which plant or animal life could not survive. Thus, many of the products that have replaced dibasic lead phosphite in these applications are powder stabilizers. A further complication arises in situations where vinyl covers polyurethane foam. The conversion of the urethane intermediates to expanded thermoset foam is catalyzed by a system that employs polyamines (diethylene triamine, triethylene tetramine, etc.) The residual catalyst is highly migratory. Traces of HCl catalyze the air oxidation of polyamines into strongly colored products (often pink); the effect being referred to as "amine stain." The urethane foam in question could use dibutyltin dilaurate (DBTDL) or stannous octoate instead of a polyamine. The frankly asinine choice of the latter probably reflects the previous use of dibasic lead phosphite, an excellent inhibitor of amine stain, in the PVC layer. Polyamines would likely have been abandoned in favor of tin catalysts had it not been for the fortuitous observation that the above chromophore formation does not occur in the presence of perchlorate anion. It was once thought that perchlorate preferentially oxidized the amines to colorless amine oxides. Reagents known to do this, such as perborates, are, however, ineffective versus amine stain. It is more likely that the perchlorate anion complexes polyamines, inhibiting oxidation, particularly to cyclic species.

Two approaches have been used in lead replacement stabilizers. The earlier was to use a stabilizer based on a hydrotalcite that contains perchlorate anion (in partial replacement of carbonate) such as Mark® 6087 ACM or Alcamizer® 5 (Kisuma). This can be combined in one product, such as Therm-Chek® 6581, PlastiStab® 2554, and Amfine® CPS-507. The alternative is to use a two-part stabilizer, one of which is a powder dispersion of hydrotalcite perchlorate, or of sodium or calcium perchlorate, such as Mark® 6045 or 6055, ThermChek® 720, and PlastiStab® 2431. There are also liquid perchlorate boosters, such as Reagens CL-510. In either case, 0.5–3 phr of the perchlorate-containing entity, depending on activity level, is typically used. Stabilizers recommended for two-part use with the above perchlorate sources include Mark® 6708 and 6711, PlastiStab® 2554, Therm-Chek® RC79L, Reagens B-NT series, and Interstab® BZ-4922. These stabilizers can also be used with filled compounds for automotive exterior use, such as extruded and injection-molded body side moldings; some suppliers have specific products for these uses, such as Mark® 6717, and variations in the Reagens B-NT series for molded, coated, and calendered applications.

An interesting spin-off of the above stabilizer development was the finding that perchlorates provide improvement in color retention in a variety of flexible vinyl compounds. The formulator faced with such a need should consider using an "instrument panel" stabilizer as a booster. Another area where they may prove useful is in compositions free of phenol content so as to resist discoloration from oxides of nitrogen.

4.4.1.3 Powder Boosters Why would one use a powder stabilizer as a "booster" for another powder or liquid stabilizer? Why not just use the optimum level of the best stabilizer? In the above case of stabilizers to combat amine stain, simple perchlorate salts are hygroscopic. It is preferable to keep their powder dispersions separate from other components prior to mixing. There is, in addition, a practical advantage. The other stabilizer component can be used elsewhere in automotive interior applications and perchlorate added only for those cases where contact with perversely catalyzed urethane foam is foreseen. The routine use of powder boosters is similar. It is often desirable to use one stabilizer, typically a liquid, throughout the plant, or at least in one section. It is often convenient to meter a standard amount into every batch and to adjust for slightly different products by adding a powder booster. Often these are lubricating and are added with other lubricants after plasticizer absorption and filler dispersion. In some cases, the addition of a liquid stabilizer with the resin and a powder booster with lubricants provides a synergistic effect that would not be found simply by increasing the level of the former. The optimum powder booster for a liquid stabilizer is often the powder recommended as the primary stabilizer for that application.

4.4.1.4 Food-Grade Powders A common choice for high-clarity extruded or calendered vinyl film for food packaging is a "high-zinc" Ca/Zn powder. These typically have 3–3.5 Zn/Ca ratios (weight percent). The following is a starting-point recipe:

FOOD-GRADE FILM

PVC	100
Plasticizer	20–40
ESO	5–15
Phosphite (TNPP)	0.5–1.0
Stearic acid	0–0.25
Stabilizer	0.5–1.0

Recommended Ca/Zn stabilizers include Mark® QTS, Therm-Chek® SP 239 and SP 1795, Baerostab® B 406, and Interstab® CZ-19A. Packaging films may also include additives to reduce fogging from moisture condensation, such as Marklear® AFL-3. A further application is in extruded beverage tubing. Some manufacturers find it convenient to use Ca/Zn pastes dispersed in plasticizer instead. Products of this type include Mark® 152M, Therm-Chek® 6220, and Interstab® CZ-11, the latter also containing an antifogging additive. For extrusion of blown film, such as for bottle cap liners, a foaming activator can be included, as in Interstab® CZ-11D. As mentioned in Section 4.1, if radiation sterilization is anticipated, the choice of antioxidant must be appropriate. Some suppliers offer special grades for this purpose, such as Interstab® GS-4571.

4.4.1.5 Flooring Components Floor tile comprises composition tile, which may have a non-PVC backing, and homogeneous or "solid vinyl" tile. Filler loadings of calcium carbonate (mixtures of different size grades) and plasticizer reduce the resin content to 15–22 percent in the former and to about 40 percent in the latter type. Composition tile is stabilized typically with inventions of the various flooring suppliers. It is usually calendered, and with the low resin level, requires tackifying additives to keep the composition adequately adhered to the rolls. Stabilizers should not interfere with the effects of tackifying resins, and thus should be nonlubricating. A common ingredient is melamine, an HCl scavenger of modest effectiveness. Trace levels of stearates can be accommodated, but common practice is to use blends of magnesium and zinc oxides with benzoic acid, particularly if PE200 is used for color retention. Roll adhesion is improved with substitution of epoxy resin for ESO as a costabilizer. Stabilizers are used at 4–5 phr and must, therefore, be of low cost. As mentioned, most are proprietary, having been developed by, or for, flooring manufacturers. Homogeneous tile typically uses Ba/Zn or Ca/Zn powders or liquids. Powders recommended include Mark® 6091, Baerostab® B 634, PlastiStab® 2156, and Therm-Chek® SP 391. These layers may then be coated with foamed plastisol and clear topcoat layers, which normally use liquid stabilizers. This is also the case with continuous sheet flooring made in a series of several plastisol coatings.

4.4.1.6 Extruded and Calendered Products A variety of filled articles conveniently use powder stabilizers. At one time Ba/Cd powders, they are now mostly Ba/Zn, used in the range of 2–3 phr, and often referred to as general purpose powders. For extrusion applications, suggested products include ThermChek® SP 346, Mark® 6705 and 6711, Interstab® BZ-4922, Halstab® 2560, and Baerostab® B 472. The conversion from cadmium to zinc has typically lowered plateout found on extruder dies and calender rolls. Tendency to plateout increases with increasing density; the use of lighter metals is beneficial. The above stabilizers can also be used in calendering operations. In addition, specifically recommended products include Mark® 6734 and 6729, and PlastiStab® 2165, a Ca/Zn powder.

4.4.2 Liquid Stabilizers

Established practice in the United States is to prepare solutions of metal salt intermediates and blend these with liquid phosphates and, in some cases, ESO, while dissolving powder ingredients, such as antioxidants. The reasons for this approach derive from industry conditions. Flexible vinyl processing is subject to great variation in operating procedure, reflecting a broad range (and age) of equipment in use. Details of processing are considered secret (regardless of whether innovative or the reverse), and few ingredient suppliers are permitted to witness the operations. The inevitable consequence is a vast number of liquid stabilizers adjusted to individual requirements. This leads to the necessity of being able to create many products rapidly, favoring the liquid blend approach.

In other parts of the world, there is closer cooperation between suppliers and manufacturers, leading to more standardized equipment and a greater willingness to adapt details of processing to suit optimum formulations. As a result, the number of liquid stabilizers is much smaller and suppliers are able to custom-make a number of Ba/Zn and Ca/Zn products directly. There is no persuasive data that this procedure leads to more effective stabilizers.

4.4.2.1 Barium and Calcium Intermediates For many years, barium-containing liquid stabilizers were based on barium nonylphenate, prepared by reaction of barium hydroxide monohydrate with nonylphenol in solvent, with removal of the water of reaction under vacuum. The course of the reaction can be followed by measuring the quantity of water collected. The products of reaction in stabilization are barium chloride and nonylphenol, a fast acting (if not very permanent) antioxidant, particularly in concert with phosphites. Stoichiometric reaction of the ingredients leads to "neutral" barium nonylphenate, in solution, an amber liquid containing 10–15 weight percent Ba. This is a useful intermediate for stabilizers sold as blends with ESO, or intended to be blended by the user prior to addition to the mixer. An alternative is to react barium hydroxide with insufficient nonylphenol for complete conversion while removing the water of reaction, and then to introduce carbon dioxide to complete the neutralization. Such products, dark liquids containing 23–28 weight percent Ba, are referred to as "overbased" barium nonylphenates, and formed the basis for "high-efficiency" Ba/Zn liquids. The structure of the microdispersion that is formed has not been reported in any detail. Overbased barium (or calcium) intermediates are not compatible with ESO or other liquid multifunctional ingredients, separating into phases. With suitable choice of solvent, they can be compatibilized with costabilizers having a single epoxy group, such as epoxy tallate esters. For low-VOC products, residual solvent can be removed under vacuum while being replaced with phosphite costabilizer.

Neutral barium octoate has also been produced for many years from octoic acid and barium hydroxide. A clear mobile liquid in solution, this intermediate (10–12 percent Ba) finds use in phenol-free ESO Ba/Zn blends suitable for flooring and wall covering use. In recent years, the use of overbased barium carboxylates has expanded greatly. Such products, typically 34 percent Ba, are now the basis for most high-efficiency liquids. The high concentration of metal results in the barium intermediate requiring only 15–20 percent of the "space" available in a liquid stabilizer to provide an effective level, leaving more room for phosphite costabilizers and other ingredients.

Neutral and overbased calcium carboxylate liquids are similarly prepared. Because of the ratio of atomic weights, the concentrations (percent Ca) that can be reached are about one-third that of barium. A general supposition is that Ca/Zn liquids are not as effective as their Ba/Zn counterparts. This is no longer axiomatic. When combined with zeolite or hydrotalcite based booster, activity may be completely equivalent. In addition, the use of light metals minimizes plateout and, in clear compounds, haze. Added to this is the perception of a less hazardous formulation. Ca/Zn stabilizers have acute oral LD50 values in laboratory animals of greater than 5000 mg/kg of body weight, a category usually thought of as nontoxic. Barium-based stabilizers are in the range of 2000–5000 mg/kg, considered slightly toxic. Common household potential hazards, such as aspirin, have lower LD50 values. Nevertheless, there is no point adding hazardous ingredients where nontoxic equivalents can be used. Thus, in new applications, Ca/Zn stabilizers should be investigated first. There has been some use in the past of strontium in place of barium because of its lower toxicity and comparable activity. Improved, lower-cost Ca/Zn stabilizers appear to have made this obsolete.

4.4.2.2 Zinc Intermediates Cadmium intermediates had the advantage that cadmium oxide can be reacted with carboxylic acids using a liquid phosphite as the reaction medium, with recovery of almost all of the water of reaction under vacuum. Zinc oxide is too reactive a phosphite hydrolysis catalyst for this procedure; it is reacted with carboxylic acids in solvent. It should be noted that new hydrolysis-resistant phosphites may revive the practice of synthesis in an ingredient rather than in a solvent. The most common intermediate is easily overbased, not as the carbonate but as the hydroxide. It is run in the range of 16–23 percent Zn, 16 percent being "neutral," higher levels overbased. All are sold commercially, for example Baerostab® B 343 (16 percent), L 210 (19.5 percent), and L 230 (23 percent). Such products are used at low levels with ESO and phosphates as the stabilizer system in medical and laboratory tubing. In low-VOC stabilizers, the reaction solvent is removed under vacuum as liquid phosphite replaces it. For increased lubrication, oleic acid, or mixtures of octoic and oleic, may replace octoic acid.

Zinc carboxylates have considerably increased catalytic ability as compared with cadmium. This extends in a positive sense to promotion of the costabilizing effects of phosphites and epoxidized oils, and to need for lower levels (also from its lower atomic weight). Thus, the overall amount of Zn in a liquid stabilizer is likely to be in the range of 1–2 percent, whereas Ba/Cd and Ba/Cd/Zn liquids used Cd levels often reaching 5–10 percent. The associated disadvantages of Zinc versus cadmium are an increased tendency to fail catastrophically instead of gradually, referred to as "zinc burn." In addition, zinc salts catalyze hydrolysis of phosphites and promote condensation of the chlorohydrin products of the reaction of ESO with HCl, as well as the development of chromophores from the oxidation of antioxidants. As a result, Ba/Zn and Ca/Zn liquids must be protected from moist air. Some users employ inert gas blankets over liquid stabilizer tanks.

There has been occasional use of stannous tin compounds, such as the readily available stannous octoate, in place of, or in conjunction with zinc. In such cases, antioxidant protection is needed to prevent oxidation to tin(IV).

4.4.2.3 Organophosphites The reactions of phosphites in PVC have been discussed recently by technologists at Chemtura[24] and Dover Chemical.[27] All organophosphites decompose hydroperoxides formed during oxidation, limiting oxidative degradation and extending processing time. They are, in addition, metal chelators, lowering the chance of plateout, particularly of barium salts. All can react hydrolytically with HCl, but it is preferable if HCl scavenging is taken care of otherwise. There are two further reactions of major interest in PVC. One is reaction with zinc chloride:

$$\mathrm{ZnCl_2 + 2(RO)_3P \rightarrow Zn[O{-}P(OR)_2]_2 + 2R{-}Cl} \qquad (35)$$

The reaction product is a much weaker Lewis acid than zinc chloride. Although it is hoped that the stabilizer will direct HCl to calcium, barium, or zeolite, in due course some zinc chloride will occur. Reaction (35) provides additional processing safety. Both reactions (35) and (36) require that at least one RO— group on phosphorus be alkyl rather than aryl, the aromatic C—O bond being too strong, under all but the most extreme conditions, to be broken in these reactions.

$$\mathrm{C{=}C{-}C{-}Cl + (RO)_3P \rightarrow (RO)_2P(O)C{-}C{=}C + R{-}Cl} \qquad (36)$$

Reaction (36) was discovered by Arbuzov more than a century ago (not with PVC). It reflects the strength of P(III) as a reducing agent, the product, P(V) bearing a P═O bond. This is the primary color retention contribution of the phosphite component. Reaction (36) is catalyzed by zinc and cadmium salts, and probably by stannous compounds.

The most commonly used phosphite is diphenyl isodecyl (DIDP). In reactions (35) and (36), trace amounts of isodecyl chloride are formed and volatilized. DIDP (not to be confused with the plasticizer DIDP; the phosphite is also referred to as DPDP and DPIDP) is highly compatible with phthalate plasticizers. It is available as Doverphos® 8 (Dover Chemical) and Weston® DIDP (Chemtura). A slightly higher phosphorus level, 9 versus 8.3 percent, can be gained by using diphenyl isooctyl phosphite (Doverphos® 9, Weston® DIOP) at the expense of higher volatility. With plasticizers less polar than phthalates, such as DOA, it is preferable to use phenyl diisodecyl phosphite (Doverphos® 7, Weston® PDDP). With one instead of two phenyl groups, PDDP is less reactive to nitrogen oxides. The latter form a brown discoloration with amines and phenols even in trace quantities, such as from phosphite ester hydrolysis. Triisodecyl phosphite (Doverphos® 6) does not react with oxides of nitrogen, and finds use in flooring and wall covering despite being less effective than the above aryl–alkyl phosphates. Trilauryl phosphite (Weston® TLP) is in the same category.

FDA-sanctioned applications were limited for many years to trisnonylphenyl phosphite (Doverphos® 4, Weston® TNPP, Interstab® CH-55, PolyGard®). This aryl phosphite cannot undergo the Arbuzov reaction and thus is of limited value in PVC. Its major use is in protection of elastomers such as NBR from oxidative degradation prior to compounding. This application led to broad FDA sanction. As a result, TNPP has been used widely in medical and food-grade flexible PVC applications, where it is better than no phosphite at all. Recently, Dover Chemical has introduced a cumyl-based diphosphite, Doverphos® S-9228, for which broad FDA sanction has been applied, and which would be much more suitable for PVC than TNPP.

In clear flexible compounds, phosphite hydrolysis can lead to haze and, in printable film, to surface tension instability. For these reasons, several relatively hydrolysis-resistant phosphites have been developed. These are based on polyhydric alcohols and include polydipropylene glycol phenyl phosphite (Weston® DHOP, and Doverphos® 12), tetraphenyl dipropylene glycol diphosphite (Weston® THOP and Doverphos® 11), and diphenyl pentaerythritol diphosphite (Weston® 600 and Doverphos® 1220). In practice, these are often used in blends with phenyl and diphenyl isodecyl phosphites, particularly in liquid stabilizers directed both at clear and filled applications.

Liquid stabilizers may also contain low levels of diphenyl phosphite (Weston® DPP) specifically to reduce plateout through chelation of reaction products containing barium. The use of an active aryl phosphite such as diphenyl or triphenyl phosphite (Weston® TPP and Doverphos® 10) adds to early color and brightness, but is of little value in extended color retention as compared with aryl–alkyl phosphites that undergo the Arbuzov reaction. A liquid stabilizer composed of about half phosphite, as is common, will usually have no more than a few percent of triaryl phosphite, most often DPP, the balance either all a phenyl isodecyl phosphite, or a blend with a hydrolysis-resistant grade. The development of more sophisticated use of phosphites has been a major factor in the replacement of cadmium in mixed metal stabilizers.

4.4.2.4 Other Additives in Liquid Stabilizers

Most Ba/Zn and Ca/Zn liquid stabilizers contain costabilizers that are β-diketones or related structures. Probably the most common example is dibenzoyl methane, $C_6H_5—CO—CH_2—CO—C_6H_5$, a low-melting solid, sold, *inter alia*, as Rhodiastab® 83 (Rhone-Poulenc). It exists mainly in the keto–enol form, $C_6H_5—C(OH)=CH—CO—C_6H_5$. Inclusion of 1–3 percent in a liquid stabilizer (in which it is readily soluble) notably improves color retention. It has been generally presumed that this stems from high activity in labile chloride displacement; that is, that the anion from the enol form displaces chloride and the additive becomes part of the polymer. The evidence to support this view is not totally convincing. Such costabilizers have no effect at all on color retention with Ba/Cd stabilizers. With zinc–phosphite liquids, β-diketones tend to worsen early color. Possibly their function is to link the primary and secondary metals together more effectively than a carboxylate anion.[5] Ba(II) and Cd(II), being nearly the same size, may fit together adequately with carboxylate ligands. It is also possible that β-diketones and related additives may simply be nonmetallic stabilizers that, in combination with Ba/Zn or Ca/Zn, are effective in reversing the activation and elimination of labile chloride.

Solid costabilizers, such as benzoyl stearoyl methane, are used in powder Ba/Zn and Ca/Zn stabilizers, and in some liquids for increased lubrication and lower tendency to promote barium plateout. A number of related costabilizers have been devised; the subject has been reviewed by Burley.[28] The use of costabilizers is another factor in the ability to eliminate cadmium, taken with improvements in compounding with phosphites and use of hydrotalcite and zeolite boosters.

Most liquid stabilizers contain a reserve of carboxylic acid to replace anions lost in labile chloride displacement. These include benzoic and octoic acids in less lubricating liquids, and oleic acid in stabilizers providing greater lubrication and for facilitating air release from plastisols. Liquid stabilizers often also contain ester lubricants such as pentaerythritol adipate oleate, Loxiol® G-71 (Cognis), or glycerol monooleate (GMO, numerous suppliers). These complex with the mixed metal stabilizer, adding mobility. They may also supplement costabilizers in linking the primary and secondary metals. In the past, most liquid stabilizers contained solvents, which served to compatibilize the various components, that is, to prevent phase separation after trace hydrolysis from atmospheric moisture. This is a problem particularly with overbased metal ingredients. Liquid stabilizers based on neutral intermediates have much greater shelf stability, but strongly limit the extent to which metal salts can be incorporated simply as a result of their greater dilution. The drive to eliminate volatile organic components (VOCs) in PVC compounds has resulted in solvents being replaced by phosphite blends. These often have a compatibilizing effect. In many cases, minor amounts of specific compatibilizing agents are included. Perhaps the most popular is dipropylene glycol monomethyl ether (DPM), available as Dowanol® DPM and Arcosolv® DPM. Such agents may complex overbased metal salts and inhibit hydrolysis. The underlying chemistry of complex liquid stabilizers has received very little attention in published literature.

4.4.2.5 Liquid Stabilizer Usage Liquid stabilizers that can be used in a variety of calendering, extrusion, and molding operations with filled and clear flexible PVC compounds are referred to as "general purpose." Ba/Zn liquids in this category include Akcrostab® BZ-5043, LT-4822, and the ESO blend LT-4803; Mark® 4754, 4864, and 4878; the Baerostab® UBZ-795 series; Therm-Chek® SP175 and the ESO blend 6325; and PlastiStab® 2420. Ca/Zn liquids include Interstab® CAZ-4949, Baerostab® B-352, and PlastiStab® 3002.

Liquid stabilizers that are recommended primarily for calendering include Interstab® BZ-5282M (Ba/Zn) for roofing; Baerostab® UBZ-793 (Ba/Zn) and CX-1092 (Ca/Zn) for wall covering; ThermChek® 6274 and 6280 (both Ba/Zn), and PlastiStab® 2384 (Ba/Zn) and 4008 (Ba/Ca/Zn Trimetal™. Those suggested primarily for extrusion include Akcrostab® BZ-4975 and 5025; PlastiStab® 2402; ThermChek® 6326 and SP 1960; and Baerostab® B-685 (all Ba/Zn liquids).

Recent stabilizers recommended for general purpose applications that require very low VOC emission include the Ba/Zn liquids Akcrostab® BZ-4967, Interstab® BZ-5264 (filled only); Baerostab® UBZ-7951D and 7955D; Mark® 9302 and 9312; ThermChek® RC 298L and 453L; and PlastiStab® 2342. Ca/Zn equivalents include Mark® 9306, PlastiStab® 3002, and Baerostab® B425. In this category, but also low-fogging for automotive interiors, are Mark® 9304 (Ba/Zn), ThermChek® 1159SF (Ba/Zn), and PlastiStab® 2396.

Stabilizers for printable applications and related postfinishing, such as metallizing, include Ba/Zn liquids Akcrostab® LT-4913; Mark® 4821 and 4825; Baerostab® B-685; PlastiStab® 4008; and Therm-Chek® SP 175 and SP 210. Calcium-zinc equivalents include Akcrostab® LT-2001M and LT-4468, and PlastiStab® 3006.

FDA-sanctioned Ca/Zn liquids for food packaging and medical applications include Therm-Chek® 659 and SP 1745; Interstab® CZL-715A, 717, and 720; PlastiStab® 2221 and 2202; and Mark® 3023.

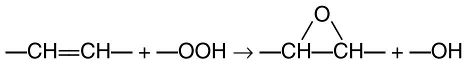
Ba/Zn stabilizers intended for plastisols (i.e., that emphasize color hold and air release) include Mark® RFD, Akcrostab® LT-4798, PlastiStab® 2380, ThermChek® 140 and SP940, and Baerostab® UBX 630 series. Those specifically pointed at flooring topcoats include Therm-Chek® SP 1363 and SP103; Baerostab® B-187; PlastiStab® 2388 and 2290; Akcrostab® LT-4801 and LT-4803; and ThermChek® 6252; the last four of these are ESO blends. Ca/Zn alternatives include Mark® 1221 and 1495C; Baerostab® B-352 and CX-1067; PlastiStab® 2031; and Akrostab® CAZ-4818 and CAZ-4949.

Products for plastisols with no detectable free phenol include Baerostab® B-1255 (Ba/Zn) and B-1265 (Ca/Zn); ThermChek® RC 457L (Ba/Zn); PlastiStab® 4013 (Ba/Zn) and 2388 (Ca/Zn); and Mark® 9305 (Ba/Zn). Low-fogging grades for automotive interiors include Mark® 4734, 4834, and 4861; ThermChek® 1159SF; and Baerostab® UBZ 1-67 (all Ba/Zn).

Liquid stabilizers for foamed plastisols (i.e., that also activate blowing agents) include Mark® 552G and 1501; the Interstab® ABC series; Akcrostab® M-823; ThermChek® 5019; PlastiStab® 2287; and Baerostab® XCT-6330 and B-1070; the latter having no detectable free phenol. Liquids for foamed plastisols are usually zinc–phosphite blends. If processing requires a higher level of stabilization, such as with long fusing cycles in filled compounds, a Ba/Zn or Ca/Zn stabilizer may be used instead, with the addition of a specific activator, usually a potassium/Zn liquid, such as PlastiStab® 2282, ThermChek® F5473, on Baerostab® CX-950. These products activate azodicarbonamide, but usually not hydrazide, blowing agents.

4.5 EPOXY COSTABILIZERS

Epoxy additives are used as combination plasticizers and costabilizers. They are formed by oxidation of an olefinic double bond to an oxirane structure by a peracid or hydrogen peroxide:



$$\text{—CH=CH— + —OOH} \rightarrow \text{—}\overset{\text{O}}{\overbrace{\text{CH—CH}}}\text{— + —OH} \qquad (37)$$

The stabilization effectiveness of the oxirane group derives both from reaction with HCl and from metal-catalyzed displacement of labile chloride from the resin (see Section 4.4). The role of an active metal, such as zinc, cadmium, or tin, and an epoxide group, in stabilization by Frye–Horst labile chloride displacement was first demonstrated by Anderson.[25] It underlies the epoxide–metal stabilizer synergism so often noted. It is likely that the entire stabilizer system—stabilizer, epoxide, and phosphite—is coordinated and travels together, perhaps with the epoxide accepting chloride displaced by phosphite. In stabilization systems using zeolite or hydrotalcite costabilizers, epoxides are often of little or no value. In such cases, the stabilizer–phosphite complex may act as an efficient vehicle for transfer of chloride to the inorganic acceptor. In rigid compounds, organotin stabilizers behave in an analogous manner, not reacting with HCl but transferring chloride effectively to zeolite, hydrotalcite, or calcium stearate. This makes possible their use at very low levels. It is in contrast to the function of lead stabilizers, which both transfer and react with chloride—thus being both primary and secondary stabilizers in one. Epoxides are, as a result, of little value with lead stabilizers.

As plasticizers, certain epoxides impart permanence similar to polymeric plasticizers and, in some cases, impart good low-temperature properties and low plastisol viscosity. Several types of epoxy plasticizer/costabilizers are in use. The most popular, because of the balance between performance and cost, is epoxidized soybean oil, usually abbreviated ESO (occasionally EPO). ESO is a mobile FDA-sanctioned liquid, CAS 8013-07-8, SpG 0.99, flash point of about 300 °C, and low color, with an octive oxygen (oxirane) content of 6.5–7.0 percent. It is sold under the trade names Drapex® 6.8 (Chemtura), Flexol® EPO (Dow), Jenkinol 680 (Acme-Hardesty), Paraplex® G-62 (C.P. Hall), PX-800 (Aristech), Polycizer® ESO (PolyOne), Plastolein® 9232 (Cognis), Plas-Chek® 773 (Ferro), Plastoflex 2307 (Akcros), and Vikoflex® 7170 (Arkema). It is also sold by Ashland Chemical, AllChem, and Sigma Group. An antioxidant is typically included. On standing in air, particularly in the presence of light, ESO will darken, increase in viscosity, lose activity and PVC compatibility, and finally resinify.

Since ESO contains molecules with more than one reactive epoxy group, it should not be blended with overbased liquid stabilizers prior to use; such blends will evolve carbon dioxide and develop an insoluble solid phase. ESO blends should be made using neutral stabilizers, that is, those in which the metals are completely reacted with carboxylate or phenolic ligands. The same restriction also applies to epoxidized linseed oil and to bisepoxides.

Epoxidized linseed oil (ELO), CAS 8016-11-3, provides at higher oxirane content, usually at slightly higher cost. It is also FDA-sanctioned for use in PVC for indirect food contact. It is a mobile liquid, with SpG 1.03, flash point of about 300 °C, and low color, with an oxirane content of 9–10.5 percent. It is sold under the trade names Drapex® 10.4, Flexol® LOE, Jenkinol L950, and Vikoflex® 7190. In most cases, performance versus ESO does not justify a cost premium. In some instances, although aging problems are similar, it has been found to provide better shelf life. ELO in place of ESO provides a higher level of resistance to extraction by hydrocarbon solvents but is worse with soapy water extraction.

Epoxidized tall oil esters (EPT) can be compatibilized with some overbased liquid stabilizers to form convenient blends. Epoxidized mixed (mainly octyl) alkyl esters of tall oil (mainly oleic and linoleic acids) are useful in lowering plastisol viscosity as compared with ESO or ELO. This results from their lower oxirane content (4–5 percent). They are mobile, more or less colorless liquids, SpG 0.92, with a flash point of 220–230 °C. Trade names include Drapex® 4.4, Flexol® EP-8, Plasthall® S-73, and Vikoflex® 4050. Because of being mostly monofunctional in oxirane, heat and light aging of the pure epoxide is considerably better than with ESO or ELO. Because of variation in the alcohol used to form the ester, these products are listed under CAS 61789-01-3 (Plasthall S-73 and Drapex 4.4) and 68082-34-8

(Vikoflex 4050). Similar products from other suppliers are listed under CAS 61788-85-0.

Ethylene and propylene glycol bisoleates and tallates are also epoxidized. Although more expensive than ESO or ELO, these products impart better heat and light aging to vinyl compounds, tend to be less volatile and migratory, and are common in severe applications such as automotive panels. They are mobile, colorless liquids, SpG 0.94–0.95, flash point 280–300 °C, with an oxirane content of 4.7–5.0 percent. Product trade names include Plasthall® S-75, Plastolein® 9215, and Vikoflex® 5075. This class should be the first choice where problems may be anticipated from migration, such as with printable films. Bisepoxides tend to be more useful with zeolite and hydrotalcite stabilizer systems than ESO. The most common CAS listing is 68609-02-7.

Another type of epoxy additive used in flexible vinyl is liquid epoxy resin, low-molecular-weight bisphenol A with glycidyl end groups, CAS 25068-38-6, a modestly viscous liquid with SpG 1.17 and flash point about 250 °C. The product is a combination tackifier and costabilizer, useful in calendering overfilled compositions such as floor tile. Suitable grades are sold as Epon® 828 (Hexion), Therm-Chek® 909 (Ferro), DER 331 (Dow), Cycom® RTM 875 (Cytec), Epotuf® 37–151 (Reichhold), and Araldite® B41 (Huntsman). Huntsman also supplies liquid epoxy resins containing predispersed additives such as antimony oxide (Araldite 103). A number of Ferro pigments are also available predispersed in liquid epoxy resin.

At relatively low levels of epoxide, less than 5 phr, assuming an efficient heat stabilizer and reasonable phosphite content, the percent oxirane content of the epoxide is largely insignificant, and the choice of type is made for other reasons. If an epoxidized oil is used as an active plasticizer, 5–10 phr or higher, then percent oxirane content enters into extent of color hold, particularly with low metal stabilizer content. This, taken with their FDA sanction, enters into the choice of ESO or ELO in applications such as medical tubing, where the stabilizer system comprises epoxide, phosphite, and minor amounts of a zinc carboxylate catalyst.

4.5.1 Epoxy Plasticizers

Epoxidized additives are generally used in the range of 1–5 phr, as plasticizing costabilizers. They can be used at higher levels in plasticizer blends, with polymerics to lower overall cost without substantial loss in performance, and, depending on market fluctuation, to replace some of the more expensive monomeric plasticizers. With efficient heat stabilizers, such blends can run as high as 25–30 percent of the plasticizer content. Above this level, heat and light aging performance tends to decline. As compared with polymeric polyesters of medium molecular weight, ESO and ELO, prior to compound aging, provide similar resistance to staining, exudation, migration and volatile loss. This will extend through service life to the extent that the stabilization system can make up for their not having the built-in aging resistance of conventional polymeric plasticizers. It should be noted that epoxy plasticizers are excellent food sources for fungi and bacteria (see Section 4.7.2). Blends of up to one-third epoxidized oil have been used in refrigerator gaskets and cable jackets.

Epoxy tallate esters are good low temperature plasticizers, comparable to DOA in effect, with lower volatility and migration characteristics. Blends of 25–30 percent EPT with low-temperature plasticizers have been common. Epoxy plasticizers in general have low fogging tendency. Automotive interior usage has centered on bisepoxides because of their superior light resistance.

The most common problem associated with use of epoxides as plasticizers has been development of incompatibility during aging, leading to migration, spew, and development of a tacky surface in the presence of sunlight and particularly in the presence of nitrogen oxides, the latter reacting to form incompatible condensation products. This is minimized by use of epoxides having low residual unsaturation (low iodine numbers), efficient stabilizer systems, and protective fillers. In general, bisepoxides yield the best retention of compatibility, followed by epoxy tallate esters.

In typical plastisols, epoxy tallate esters and bisepoxides yield viscosities comparable to general purpose plasticizers with lower tendency to build on standing; higher-molecular-weight ESO and ELO yield increased viscosity. The most common usage has been in coated fabrics, with 10–20 percent of the plasticizer content as epoxy tallate ester in highly flexible compounds, 5–10 percent in stiffer products.

Bis-epoxides are quite good secondary plasticizers in vinyl/NBR blends, being active in both polymers, 20–30 percent of the plasticizer content often used with high efficiency mixed metal/phosphite stabilizers. With rigid vinyl compounds that are actually blends with acrylic or other modifying polymers, when mixed metal stabilizers are used, 1–3 phr of epoxy costabilizer is typical. Use with organotin or lead stabilizers has not generally been advantageous.

4.6 ULTRAVIOLET LIGHT STABILIZATION

Returning to Reaction (1), the loss of a proton from the polymer to form a radical, initiating oxidation, why can it matter whether the loss is caused by shear, abstraction by oxygen or by another radical, or from the input of a quantum of energy from a photon of UV light? Why are standard antioxidant systems not adequate? One factor is light intensity. There tends to be too many points of initiation for a repetitive additive to prevail. An extreme example of this effect is ignition. Although combustion is a radical chain reaction oxidation, too many sites are initiated for the combination of primary and secondary antioxidants to have much effect. This is not always true. If the availability of fuel, C—H bonds, is limited, for example, in silicone polymers, certain antioxidants will add to flame resistance. Similar effects are found in moderately flame retarded polyolefins.

Another factor is that primary and secondary antioxidants are typically themselves not UV light-resistant. The most important factor, however, relates to the mechanism of antioxidant action. The success of the antioxidant system derives from there being a lower energy barrier for the radical formed to complex with the antioxidant than to be oxidized to reaction products. The quanta of energy delivered by UV light are sufficiently energetic to swamp the difference in energy barriers. This effect can be combated in two ways: by absorbing UV light and dissipating the incoming energy as heat, the conventional approach, and by defeating the initiation that conventional antioxidants cannot handle with new types of additives.

4.6.1 Conventional UV Light Absorbers

The most effective UV light absorber is fine-particle carbon black. It absorbs UV (and visible) light across the spectrum and is excited electronically. The rapid movement of electrons in excited energy states dissipates the absorbed energy as heat. All fillers of high dielectric constant (easy polarizability) have this effect; in practice, carbon black and titanium dioxide are the only ones commonly used. The effectiveness of UV light absorption increases with the fineness of particle size. Although metal powders are also effective, as in metal filled coatings, vacuum metallization does not provide a sufficient barrier to UV light-initiated degradation of PVC. Fillers of relatively low dielectric constant, such as calcium carbonate, absorb or reflect some UV light; filled compounds degrade more slowly than clear, but still require additional protection for severe exposure. The use of fine particle carbon black or titanium dioxide (or both) is effective, but limits the compound to black, white, or shades of gray—often an unacceptable constraint.

Dibasic lead phosphite is also a UV light absorber. It has greater effect than calcium carbonate or other opaque stabilizers such as tribasic lead sulfate. It is likely that the protection it offers PVC comes from its combination of stabilizing, phosphite antioxidant, and light absorption properties. In outdoor use, such as in roofing, it is typically combined with fine particle carbon black or titanium dioxide (or both in gray compounds). It is possible that dibasic lead phosphite can transfer energy to carbon black or titanium dioxide when in close proximity. In photosynthesis, it is known that carotenoid pigment light absorbers, which absorb in the center of the visible spectrum, transfer energy to chlorophylls, which absorb at both ends of the visible. The carotenoid and chlorophyll molecules are in close proximity, and it is thought that the energy transfer may involve tunneling though the barrier separating them, similar to conduction through thin layers of polymer separating particles of conductive carbon black. In general, the combination of protection mechanisms versus UV light-initiated degradation is likely to be synergistic.

Conventional UV light absorbers are analogous to inorganic fillers of high dielectric constant. An incoming photon delivers a quantum of energy, driving the UV light absorber into an excited electronic state. The structure of the additive is such that the excited state is resonance-stabilized, enabling it to persist long enough to dissipate energy in vibration as heat. One of the oldest groups of organic UV light absorbers is the class of 2-hydroxybenzophenones. These compounds absorb strongly in the range of 295–400 nm (the UV light range), particularly at 310–330 nm, where PVC is most sensitive. The excited state is stabilized by keto–enol tautomerism between the ketone and phenolic —OH group. A problem common to this class of UV light absorbers is that in the presence of Lewis acids, such as zinc chloride formed from the action of mixed metal stabilizers, there is absorption of light above 400 nm, in the blue region, leading to a yellow tint on aging. Another is that hydroxybenzophenones are subject to oxidation and, therefore, should be used with an antioxidant. The oxidation products are often strongly colored.

An advantage to this class of UV light absorbers is their relative low cost, leading to some use in PVC despite their not being ideal. The most commonly used example is 2-hydroxy-4-methoxybenzophenone, Cyasorb® UV9 (Cytec), Uvinul® M-40 (BASF), UV-Chek® AM 300 (Ferro), *inter alia*. Similar products include 2-hydroxy-4-octoxybenzophenone, Chimassorb® 81 (Ciba), and the dodecoxy analog, Inhibitor DOPB® (Eastman). The latter two, with longer alkyl side chains, are preferable in blends with less polar polymers such as EVA. A combination phenolic antioxidant/UV light absorber related to this class is UV-Chek® AM-340 (Ferro).

Generally more useful in PVC is the class of hydroxyphenylbenzotriazoles. In this case, the excited state is stabilized by development of negative charge on the phenolic oxygen and positive charge on a triazole nitrogen, possibly to the extent of actual proton transfer. (Pictorial representations of excited states are likely to be oversimplifications.) Benzotriazoles absorb very strongly in the UV region and are more resistant to oxidative discoloration than benzophenones. On the other hand, they are notably more expensive. The most common example is 2-hydroxy-5-methylphenylbenzotriazole, Tinuvin® P (Ciba). Also used in PVC is the octylmethylphenyl analog, Tinuvin® 329 and UV 5411 (Cytec) the t-butylphenyl analog, Tinuvin® 320, and the t-amylphenyl analog, Tinuvin® 328. All of these, in particular, the last three types, are antioxidants as well as UV light absorbers. Benzotriazoles typically have much greater persistence in PVC (and other polymers) than benzophenone UV light absorbers.

The class of conventional UV light absorbers includes cyanoacrylate esters; their excited states are resonance-stabilized but not easily oxidized. The product most commonly used in plastics is ethyl 2-cyano-3,3-diphenylacrylate, Uvinul® N-35. The octyl ester, Uvinul® N-539, has been suggested for use in PVC. Another group is that of oxanilides, the most common example being 2-ethyl-2′-ethoxyoxanilide, Sanduvor® VSU (Clariant). Oxanilides are also metal scavengers and might be used where migration of transition metal prodegradants is anticipated, as in wire coverings.

Probably all of the "conventional" UV light absorbers have antioxidant capability and function not only to dissipate incoming energy but also to interfere with subsequent reactions leading to oxidation. This is also true of a class of additives known as "quenchers," which catalyze the dissipation of energy (as heat) by UV light-excited states. The most common example is nickel dibutyl dithiocarbamate, Isobutyl Niclate® (RT Vanderbilt). These compounds are, however, also secondary thio-type antioxidants and absorb strongly in the UV region. Thus their function is likely complex. In addition, useful additives have been limited to nickel compounds, leading to a slight green coloration.

4.6.2 Hindered Amine Light Stabilizers

This class of additives is characterized by the presence of an easily oxidized secondary amine group. Unlike with hindered phenols, it is intended that oxidation occur.

This can be initiated by oxygen, polymer radicals plus oxygen, or by hydroperoxy radicals:

$$R_2N{-}H + O_2 \rightarrow R_2NO^{\bullet} \tag{38}$$

$$R_2N{-}H + R'^{\bullet} \rightarrow R_2N^{\bullet} + O_2 \rightarrow R_2NO^{\bullet} + R'H \tag{39}$$

$$R_2N{-}H + R'O{-}O^{\bullet} \rightarrow R_2NO^{\bullet} + R'OH \tag{40}$$

The nitroxyl ($NO^{\bullet}$) radical formed proves highly useful. It reacts with and consumes polymer and hydroperoxy radicals and is regenerated:

$$R_2NO^{\bullet} + R'^{\bullet} \rightarrow R_2NO{-}R' + R''^{\bullet} \rightarrow R'{-}R'' + R_2NO^{\bullet} \tag{41}$$

$$R_2NO^{\bullet} + R'O{-}O^{\bullet} \rightarrow R_2NO{-}R' + O_2 \rightarrow R_2NO^{\bullet} \tag{42}$$

Thus, free-radical chain reaction oxidation is met by chain reaction termination. This scheme enables an additive that is not a UV light absorber to stabilize plastics against light-initiated oxidation. The above reaction paths do not, unfortunately, imply perpetual protection in outdoor service. To limit volatility, commercial products are most commonly low polymers or otherwise large molecules. Eventually other parts of the additive (rather than the N—H group) will oxidize. Therefore, in practice, hindered amine light stabilizers (HALS) tend to be used with UV light absorbers and often with a phenolic antioxidant/phosphate package. Although sometimes used, HALS are not optimum with tin mercaptide stabilizers, probably because the thio groups reduce the nitroxyl radical:

$$R_2NO^{\bullet} + \;{-}S{-}\; \rightarrow R_2N^{\bullet} \rightarrow R_2N{-}NR_2 \tag{43}$$

This leads not only to consumption of the valuable additive but also potential development of azo chromophores. For similar reasons, HALS should not be combined with thiodipropionate secondary stabilizers nor with nickel-sulfur quenchers.

High-molecular-weight monomeric products suggested for use in PVC include BLS® 1944 (Mayzo), Cyazorb® 3765 (Cytec), LA-77 (Amfine), and Lowilite® 92 (Chemtura). The monomeric HALS have been used in liquid color concentrates for outdoor use. Polymeric products for PVC include Cyazorb® 3346, Tinuvin® 622 LD and XT 833, Chimassorb® 944 FL, Uvinul® 5050H (BASF), Hostavin® 845 (Clariant), and Lowilite® 62.

4.6.3 Usage in PVC

White rigid tin mercaptide-stabilized PVC for outdoor use is best protected by the use of 8–12 phr of fine particle rutile (TiO_2). At this level, addition of organic UV light absorbers has little effect on color retention. This level inhibits the range of available colors. If, to enhance the effect of color concentrates, TiO_2 is held to 5–8 phr, 0.2–0.3 phr of a benzotriazole UV light absorber will prolong time to bleaching in strong sunlight. The protection will be far from perpetual. The best solution (in an all PVC construction) is to use a tin carboxylate stabilizer in the capstock plus 0.2–0.3 phr each of a benzotriazole UV light absorber and polymeric (nonmigratory) HALS. Such systems yield low delta E values after 6 months' xenon arc or 12 months' Florida exposure. This is particularly useful in brown siding capstock and window profile components. A technically better solution is to use an acrylic capstock containing benzotriazole UV light absorber plus HALS. With this approach, the siding or profile component is protected from oxidative discoloration and chalking of pigment.

In clear rigid or semirigid PVC stabilized with a methyltin or octyltin mercaptide per FDA sanction, a maximum of 0.25 phr of Tinuvin® P (or chemical equivalent) is permitted. This level is ordinarily adequate for fluorescent light exposure. For non-FDA applications, 0.3–0.5 phr of Tinuvin® 329 or UV 5411 is a common choice. If modest exposure to fluorescent light is anticipated and raw material cost is a major factor, a benzophenone such as Chimassorb® 81, Uvinul® M-40, UV-Chek® AM 300, Cyasorb® UV 531, or Inhibitor DOBP® might be used at 0.2–0.3 phr. The use of UV light absorbers in clear rigid or semirigid compounds is often to protect the contents rather than the PVC from degradation. This is true in areas where Ca/Zn stabilizers are used in place of organotins.

An important use in flexible PVC is in roofing. Such compounds typically are formulated either with titanium dioxide or fine-particle carbon black (e.g., ASTM grade N110) for UV light absorption. Performance life is improved by addition of 0.3–0.5 phr of a polymeric HALS such as listed above. Clear flexible sheet, as in pond or swimming pool liners, should use a combination of 0.2–0.3 phr each of a benzotriazole and a polymeric HALS. In FDA applications, use is again restricted to a maximum of 0.25 phr of Tinuvin® P or chemical equivalent. Note that suppliers' literature should be checked for new approvals.

In pigmented applications, such as automotive roof coverings, best results in outdoor exposure will be found will be found with use of hydrotalcite or zeolite in place of ESO as the HCl absorber. This is also true in blends with olefin copolymers such as EVA, where scavenging of Ziegler–Natta or metallocene catalyst residues is important in preventing discoloration from their reactions with both benzophenone and benzotriazole UV light absorbers.

4.7 BIODEGRADATION

No microorganisms have yet been discovered that can metabolize PVC or other halogenated polymers. However, many plasticizers, as well as fatty acid components of stabilizers (e.g., stearates), can be metabolized. This is particularly true of ester plasticizers (and lubricants) under conditions where hydrolysis can occur. Those based on natural products, such as ESO, are particularly vulnerable. Both fungal and bacterial growth are unsightly and limit the practical life of articles such as shower curtains;

that is, the articles may be discarded due to revulsion even though they are still functional. In the extreme case, consumption of plasticizer and stabilizer may lead to cracking, as with unprotected vinyl roofing. Fungal damage is more prevalent than bacterial, although both can occur. Fungi metabolize by secretion of enzymes from rootlets, referred to as hyphae, which digest a wide variety of hydrolysable substances including carbohydrates, cellulose, lignin, natural products of all types, and many esters and amides. This provides a target for attack by incorporation of additives that interfere with enzymatic action by complexing or reacting with the proteins involved. The principal reactive group used is the phthalimide functionality. This group also bonds to bacterial cell walls, analogous to the action of β-lactam antibiotics, such as penicillins and cephalosporins. (The additives employed are, however, too toxic for use as antibiotics.) The most common members of this class are trichloromethylmercaptotetrahydrophthalimide, Captan® (R.T. Vanderbilt, also sold as Fungitrol® C, International Specialty Products), and the analogous phthalimide (not tetrahydro), Folpet® (Huls, also sold as Fungitrol® 11, I.S.P.). These agents also penetrate both fungi and bacteria with fatal results, probably through reaction with S—H groups on DNA and RNA. They are EPA-registered under the Federal Insecticide and Rodenticide Act (FIFRA) and should be handled as toxic materials per the pertinent MSDS instructions. In articles for indoor use, typical levels of the additives, supplied as 88 percent active powders, is in the range of 0.2–0.3 phr, with twice that level used in outdoor applications. Outdoor articles should be heavily stabilized, since phthalimides can react with HCl, and provided with UV light protection to minimize degradation of the biocide. Benzotriazole UV light absorbers are suitable; interactions with HALS products are possible although unreported. Related halogen-containing products include fluorodichloromethylthiophthalimide (Preventol®, Bayer) and hydroxyltrichlorodiphenyl ether (Irgasan®, Ciba). All of these have found use in agricultural films, shower curtains, wall coverings, shades, and upholstery. This class of biocides is useful in a variety of plastics and elastomers at the above low levels. It is likely that they migrate to the surface and therefore may be enhanced with the use of external lubricants. In some applications, the odor of the additive may be found unattractive. The use of sulfur-containing biocides with lead stabilizers is likely to lead to interaction (particularly Captan®), and should be thoroughly investigated before use in production.

The most widely used biocide in PVC has been oxybisphenoxarsine, sold as Intercide® ABF (Akcros) and Vinyzene® OPBA (Rohm & Haas). OPBA has high solubility in plasticizers and is most often sold as 2 and 5 percent concentrates. The 2 percent concentrates are commonly used at 1.5 phr in indoor, and at 2.5 phr in outdoor applications; the 5 percent concentrates at 0.6 and 1.0 phr, respectively. OBPA poisons a variety of fungi and bacteria at low concentrations. It is most likely ingested with plasticizer breakdown products and, mistaken for a phosphorus source, destroys ADP–ATP conversion processes (the usual mode of action of arsenic). Apparently, bacteria and fungi have not developed the sophisticated processes used by higher forms of life to sequester and eliminate trace levels of arsenic. The plasticizer concentrates, nevertheless, must be handled with care. OBPA is widely used in shower curtains and in a variety of outdoor applications, including automotive vinyl tops and upholstery, and swimming pool liners. These should have good UV light protection, as oxidation under hydrolytic conditions may degrade the additive. The final product, arsenious oxide (arsenic (III) oxide) is sufficiently water-soluble to lose permanency. Benzotriazoles and HALS UV light absorbers should be considered, with evaluation in the specific product. Much recent compound development has been concerned with replacement of OBPA with additives considered (particularly by regulatory authorities) to be less toxic. It is, in fact, likely that use of OBPA in North America will disappear, as has already occurred with tributyltin oxide, a powerful biocide, but one that has drawn strong regulatory reaction. As mentioned previously, the vinyl formulator must consider the effects of specific additives on public acceptance of PVC articles.

Another broad-spectrum biocide finding use in PVC is isothiazolone (2-octyl-4-isothiazolin-3-one) (MicroChek® 11, Ferro; Acticide® 45, Thor Gmbh; Micropel® IT, Troy Corp; and Vinyzene® OIT, Rohm & Haas). It is supplied as concentrates in plasticizer or in resin. These are used in plasticized formulations at about 1 phr for indoor applications, 2.5 phr for outdoor, both levels assuming a 4 percent active concentrate. At these levels, it is effective against both bacteria and fungi. For outdoor applications, again a UV light absorber should be included, as the additive is sensitive to UV light-catalyzed oxidation, the eventual product being a dark tar. HALS UV light absorbers should not be used in combination with isothiazolone biocides without evaluating potential chemical interactions. OIT concentrates in ESO are particularly useful, since the latter is an attractive food for fungi. Related products include 1,2-benzisothiazolin-3-one, Nuosept® 400 series (I.S.P.) and *N*-butyl-1,2-benzisothiazolin-3-one, Vanquish™ 100 (Arch Chemical, Inc.)

It is likely that isothiazolones act similarly to phthalimide biocides, interfering with enzymatic metabolism of nutrients. Isothiazolones are toxic to aquatic life, and should not be used in liners for ponds for raising of fish or plants, or in agricultural films.

Another related product is dichloroisothiazolone (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one), sold as Acticide® DT (Thor Gmbh), and Vinyzene® DCOIT (Rohm & Haas). Dichloroisothiazolone is a colorless liquid with much improved resistance to UV light than isothiazolones. It is similarly toxic to aquatic life, and should not be used in agricultural films or in pond liners. It is a broad-spectrum biocide, effective against fungi, bacteria, cyanobacteria, and green algae. It is also an insecticide. Its use in compositions containing HALS UV light absorbers should be investigated for negative interactions. Levels of 0.05–0.1 phr (pure basis) are effective.

There is increasing use of zinc pyrithione (Zinc Omadine®) in PVC because of its relatively good resistance to heat aging and UV light exposure.[29] As pointed out by Burley and Clifford, the potentially damaging effects of zinc-containing additives can be overcome using heat stabilizers containing hydrotalcite.[29] This may be the case with zeolite-based stabilizers as well. Zinc pyrithione is effective against both bacteria and fungi, probably both by interference with nutrient metabolism and, upon penetration of the organism, by disruption of ion channel flow. It is supplied (Akcros) as a 5 percent suspension in plasticizer. Use levels of this concentrate are 2.5–3.5 phr, plus 1–2 phr of hydrotalcite (to prevent zinc burn). Zinc Omadine itself is available from Arch Chemicals.

Related products include zinc dimethyldithiocarbamate (Methyl Zimate®, RT Vanderbilt). This material, generally abbreviated as ZMDC, is a common additive in sulfur-vulcanized rubber compounds, and is often formed from other rubber accelerators during the vulcanization process. It is less effective than the products listed above, but typically more permanent. Dithiocarbamates typically darken on exposure to UV light.

4.7.1 Use in Rigid PVC

Until recently, biodegradation of rigid PVC was not a problem, because of the lack of available nutrients. Calcium stearate is biodegradable, but is either present at too low a level or unavailable at the product surface. This has changed with the development of PVC wood fiber composites. Sufficient wood is exposed to support microbial growth. The problem is compounded by the relative insolubility of the above biocides in unplasticized PVC; they were designed for solubility in common plasticizers. Therefore, the most useful procedure is to coat the wood fiber with the biocide prior to incorporation into the PVC compound. Usually, the biocide may then be combined with a tannin stain inhibitor and compatibilizing agent in a single water-based coating. One of the most effective choices of current biocides is DCOIT, because of its UV light resistance. If the PVC stabilizer system is zinc-resistant (i.e., used a combination of organotin with hydrotalcite or zeolite), DCOIT can be supplemented with Zinc Omadine for increased permanency. A blend of *N*-butylbenzisothiazolone and Zinc Omadine, (Vanquish™ SL-10) is available from Arch Chemicals. In cases where extraction into soil or runoff water is a critical factor, a useful product to consider is Irgaguard® F3000 (Ciba), thiazolylbenzimidazole, which has relatively low water solubility and good resistance to UV light, typically at 0.3–1.0 phr.

A possible alternative is to coat cellulosic nutrients such as wood fiber with a hydrophobic layer; it is the combination of nutrient and moisture that supports microbial life. It has been reported that coating wood fiber with a water-based acrylic containing low molecular weight PTFE provides equivalent protection to a range of biocides.[30]

4.7.2 Use in Flexible PVC

The primary nutrient in flexible PVC is the plasticizer. Epoxidized natural oils are easily metabolized by a variety of bacteria and fungi. In some cases, liquid epoxy resins can be substituted for, for example, ESO, improving microbial resistance. Since epoxy resins usually add tack, revision of the lubricant system may be required. In filled or pigmented compounds, it would be preferable to use an acid absorber such as hydrotalcite or zeolite in place of ESO, or a stabilizer system based on such ingredients. This is also possible in translucent compounds such as shower curtains. Polyol components of stabilizers, such as pentaerythritol, are also nutrients. As with rigid PVC/wood fiber composites, the ideal stabilizer would be a combination of organotin carboxylate and hydrotalcite or zeolite. In many cases, the required material cost will milicate against this choice. It may be noted in passing that neither lead nor barium/cadmium stabilizers add to microbial resistance; zinc and tin compounds are, in this regard, more toxic.

Aliphatic ester plasticizers, such as adipates and sebacates, are almost as vulnerable as ESO to microbial attack. Newer materials in this class, such as esters of cyclohexane carboxylates, are more resistant (e.g., is Hexamoll DINCH®, BASF). Two factors are involved: the tendency of the plasticizer to bleed to the surface, and its ease of hydrolysis. Thus, greater resistance, for example, among adipates will be obtained with DINA versus DOA. Polymeric polyester plasticizers are more resistant than monomeric for the same reasons.

Aromatic esters are more resistant. Resistance to microbial attack among phthalate plasticizers follows resistance to hydrolysis—that is, essentially to heat stability. Aliphatic phosphate plasticizers are similar in microbial resistance to phthalates; aromatic and halogenated phosphates and chlorinated paraffin appear to be inedible. Usually, plasticizer choice is dictated by other factors, thus requiring use of biocides.

In filled or pigmented indoor applications, OBPA should be replaced with Zinc Omadine or a competitive zinc-based biocide, if the stabilization system permits the use of zinc-based additives. This category includes flooring, wall coverings, bath mats, and vinyl sheeting for die-cut goods. In translucent articles, such as shower curtains and clear topcoats, and those where zinc-based additives cannot be tolerated, the current best choice is an isothiazolone biocide. Where maximum light stability is needed, dichloroisothiazolone is preferable. The latter is also a good choice for outdoor applications such as automotive exterior trim and vinyl tops, window gasketing, and outdoor furniture components. Where runoff into water systems is a factor, as in pond liners, tarpaulins, roofing, garden hose, and outdoor wiring, phthalimide biocides should be evaluated. If permanent outdoor use is contemplated, combinations of the above with zinc-based biocides should be the first choice.

The above biocides are generally also available as emulsions for use with vinyl latex. These may be supplemented for protection before use with a water-soluble biocide such as dimethoxane (DXN, Dow Chemical).

4.7.3 Test Methods

ASTM D 3083, Flexible PVC for Pond, Canal and Reservoir Lining Test specimens are buried in microbial-rich soil (e.g., per ASTM D 5526) for 30–60 days at 35 °C, and then examined for fungal growth, weight loss, and decrease in physical properties. This is a reasonable test method for the typical PVC formulator. As with all of the laboratory methods, it must be supplemented with field exposure in order to determine fitness of the product for the intended service. The following two test procedures should be carried out only by trained technologists.

ASTM G 21, Resistance of Polymeric Materials to Fungi Test specimens are placed on a non-nutrient agar composition and inoculated with a suspension of spores of five specific fungi. After 21 days at 28 °C, 85 percent relative humidity, the specimens are rated as to fungal growth. In a variation called for in automotive specifications, dextrose or another sugar is added to the agar, making it a nutrient. After exposure, the article not only must have shown no fungal growth, but also must have inhibited growth nearby in agar. This area is termed the zone of inhibition. Although none of the fungi used is known to be pathogenic, tests should be carried out by those trained in biological procedures.

A problem with the zone-of-inhibition protocol is that success depends upon migration of the biocide, or the plasticizer carrying it, into the surrounding water-based agar. Water extraction is rarely what the user values. It reflects the difference between ASTM specifications, which are investigated and agreed on by a number of technologists, and specifications promulgated without industry-wide testing, common to some industries. The zone-of-inhibition requirement can easily be reached by adding traces of a water-soluble secondary biocide (DXN, Dow) rather than compromising choice of plasticizer.

ASTM G 22, Resistance of Plastics to Bacteria The test protocol is similar to G 21; specimens are inoculated (usually) with *Pseudomonas aeruginosa*, an opportunistic soil bacterium that is a hazard to immune-compromised persons. The zone of inhibition is sometimes determined. This should not be combined with fungus resistance testing, as *Pseudomonas* can metabolize a variety of fungi (instead of the biocide-containing nutrient).

ASTM G 29, Algal Resistance of Plastic Films Test samples are suspended in an aquarium containing algae, illuminated by sunlight-simulating fluorescent lamps. After 2 weeks, samples are examined. Algae feed by photosynthesis and use vinyl film merely as anchorage. Algae deposits then form a medium on which fungi and bacteria can grow, insulated from additives in the plastic. OBPA and isothiazolones are strong algaecides. This test is easily carried out by the vinyl formulator.

Resistance to Pink Stain Automotive Specifications Specimens are placed on nutrient agar and inoculated with *Streptoverticillium reticulum*, a harmless mold whose metabolic products include a red dye, soluble in plasticizer. After 14 days at 28 °C, samples are rated for degree of stain and extent of a zone of inhibition. This procedure should be carried out by trained persons.

4.7.4 Biodegradability

It is at times desired that vinyl articles biodegrade—or at least vanish into a landfill. Reports to date suggest that vinyl articles are immortal in landfills. Even with use of aliphatic plasticizers, degradation is limited to cracking and fracture. There are no reports of catalysts for depolymerization under landfill conditions comparable to the effects of cobalt and manganese catalysts used with landfillable polyolefin products such as trash bags. In the case of vinyl, such catalytic action would be unacceptable if accompanied by formation of vinyl chloride monomer or evolution of HCl.

What would be needed would be additives that promoted chain scission, rather than crosslinking, on oxidation under conditions of limited oxygen. This is an area that deserves study. Testing should follow ASTM D 5526, Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions. In this method, which is suitable for the typical vinyl formulator, samples are exposed to a mixture of 60 percent simulated household waste (e.g., sterilized dehydrated manure), 30 percent distilled water, and 10 percent fermenting inoculum (e.g., garden compost) at 30 °C in a dark incubator. Loss of physical properties, loss of weight, and microbial growth are observed. Gas evolution may also be determined. Cellulose controls (filter paper) typically vanish in 30 days. Biodegradable polymers such as polylactic acid (PLA) film are consumed in 5–10 days. Untreated polyolefins such as LDPE film are unchanged after 90 days.

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CHAPTER 5

Colorants for Vinyl

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5.1 COLOR MEASUREMENT

Color is the brain's reaction to the eye's perception of certain wavelengths of light. Cone receptors in the retina are sensitive to blue, green, and red regions of the visible spectrum. The brain, to generate human perception of color, carries out addition and subtraction of the response of the three color receptors. A defect linked to the X chromosome results in the operation of only two of the three color receptors, leading to red–green color blindness, typically in men. Women, with two X chromosomes, usually deactivate the defective one. Most other animals do not have cone receptors or color vision. Cone receptors require a certain level of light to operate (with some individual variability). In dim light, human perception is limited to the gray scale seen by most other creatures. Intensity of illumination is therefore a factor in color perception.

Colorant is the term given to additives that absorb part of the light spectrum, and reflect or transmit the rest. Thus, when a colorant absorbs, for example, all light

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except blue, and reflects or transmits the remainder, the brain perceives a blue color. When a colorant absorbs most wavelengths of light equally, the article appears black; when colorants reflect all wavelengths, it appears white. The absorption characteristics of the colorant are often influenced by interaction with other ingredients; the perception of color by a number of factors.

Visible light is the part of the electromagnetic spectrum between 400 and 700 nm. The ability of a pigment to absorb light at specific wavelengths can be determined using a spectrophotometer. Such spectra are not in themselves an adequate measure of color, because they do not necessarily correspond to the type of light under which the colorant is viewed, or to the human capacity to see color.

Several analytical approaches deal with these variables. They are based on so-called *tristimulus vales*, X, Y, and Z, representing what is thought to be average human response to light with intensity maxima of (about) 500, 550, and 600 nm, the blue end of the visible spectrum, the center, and the red end, respectively. These are taken as independent variables. Three dependent variables, L, a, and b, are generated from them, creating a three-dimensional color space. The variable L is proportional to the ratio of the intensity of Y, the center of the visible spectrum. Y_0 denotes the value of Y if all of the incident light received by the colorimeter were scattered. Thus, a change in L reflects a change in intensity of perceived color. The variables a and b describe color shifts towards the red and blue ends of the visible spectrum, respectively. They are obtained by measurement of the ratio of X and Z to X_0 and Z_0 (again the values that would be found with complete scattering). The specific equations relating L, a, and b to Y/Y_0, X/X_0, and Z/Z_0 depend on the system used, popular examples of which are those of Hunterlab® and CIE (Commission International de l'Eclairage). Fortunately, computerized colorimeters provide L, a, and b values directly.

Commonly, the effects of changes in three-dimensional color space are reported in a combination derived variable, ΔE, the square root of the sums of the squares of L, a, and b. Most observers can distinguish a color change of ΔE of 1–2; an experienced colorist, often 0.5. ΔE values are typically used to report color change in PVC compositions after heat aging, per ASTM E308. This has largely replaced use of the Yellowness Index (ASTM D1925) and reports of visual evaluation (ASTM D1729). The formulator should also consider changes in L, a, and b in evaluating stabilizers (as well as in characterizing the color of a compound), since color stability, usually referred to as color hold, is an important factor in stabilization. Commonly, if a ΔE value is spread uniformly among the L, a, and b factors, it will be perceived as less of a change from the original color than if it is concentrated in one of them. Some product specifications prescribe allowed values for L, a, and b.

Metamerism is the perceived change in color when conditions of viewing are altered. The phenomenon was first noted when colors were matched under artificial light and found to be different in daylight. When this occurs during visual color matching of samples of the same formulation, it typically indicates a difference in colorant. This procedure is often used for quality control analysis and pigment identification. Metamerism can be a serious problem to a formulator attempting to match a colored object (paint, paper, textile, or ceramic) based on colorants unsuitable for

PVC. Such problems often respond to blends of suitable colorants; for example, achieving a red coloration with a blend of red pigments. Metamerism may also occur with differences in angle of light incidence or reflection, and is subject to individual variability in the observer.

There are basically two types of colorants: those that are soluble in the compound (dyes) and those that are insoluble (pigments). Some pigments show slight solubility, although this is generally undesirable since solubility leads to bleeding or plateout. Both dyes and pigments are listed by their Chemical Index (CI), which provides their structure and CAS number. A listing is provided by the National Association of Printing Ink Manufacturers (NAPIM, www.napim.org) in their Raw Materials Data Handbook, Volume 4, a thorough, although expensive, source. Subsets can be found in suppliers' literature.

Colorants suitable for use in food, drugs or cosmetics are listed by the Food and Drug Administration (FDA) per Subchapter B of the Federal Food, Drug, and Cosmetic Act (www.fda.gov). They are commonly referred to by the FD&C numbers assigned by FDA.

5.2 GENERAL CONSIDERATIONS

Dyes have the advantages of high transparency, ease of incorporation, and high tinting strength. Disadvantages include tendency to migration, marginal light fastness and heat stability, and possibility of reaction with other ingredients or with degradation products such as hydrogen chloride (HCl). These tend to outweigh the advantages, particularly poor light fastness and heat stability. Nevertheless, dyes are sometimes used to tint clear rigid or semirigid PVC. Examples include CI Yellow 163 (anthraquinone type, Oracet® Yellow GHS, Ciba), CI Yellow 93 (pyrazolone type, Thermoplast® Yellow 104, BASF), CI Red 135 (perinone type, Oracet® Red GN, Ciba), CI Red 195 (monoazo type Thermoplast® Red 454, BASF), and CI Blue 13 (anthraquinone type, Oracet® Violet TR, Ciba and Thermoplast® Blue 684, BASF), and CI Blue 35 (anthraquinone type, Thermoplast® Blue 670). Interactions with stabilizers should be investigated; organotin carboxylates are generally used. Use of the above in plasticized compounds will usually lead to bleed and staining. Use in blends, such as with NBR or urethanes, is not recommended, because the dye is likely to have higher solubility in one or the other phase.

PVC is typically colored with pigments, including colors used in concentrations as low as 0.01 parts per 100 of resin (phr), and white pigments, such as titanium dioxide, sometimes used at concentrations as high as 20 phr. PVC processing requires pigments with a special set of characteristics compared with other colorant-using industries. Pigments that in themselves will not withstand processing temperatures obviously cannot be used. Pigments containing metal cations used in stabilizers (e.g., zinc) must be chosen carefully. Similarly, pigments containing amine groups (e.g., anthroquinone or azo-based) should be checked for effects on heat aging.

Some pigments are unsuitable for electrical insulation because soluble salts remain in the pigment. The electrical properties of such pigments can be improved by preparing a dispersion by a technique known as flushing. This process transfers the pigment from the water phase to a plasticizer (or oil) before drying. This wets the surface of the pigment preferentially, and the water separates into a second phase, carrying the water-soluble salts with it, and is decanted.

Pigments are supplied as fine powders. In order to improve incorporation during mixing, and to reduce dust levels, they are often predispersed. Dispersion involves breakup of agglomerates formed during drying, packaging, and storing; wetting of the binder and replacing the pigment–air interface with a pigment–binder interface; and stabilization of the dispersion to prevent agglomeration. Using a pigment efficiently for best value and end-use properties requires proper dispersion. Value reflects tinting strength in relation to cost. Tinting strength is dependent on the degree of dispersion, which requires shear in mixing. The shear levels found in mixing and processing of compounds are often not enough to result in proper pigment dispersion. Specialized equipment, such as three-roll ink mills, pebble mills, high-intensity high-speed mixers, and impingement mills, are used to prepare pigment dispersions. Wetting agents and surfactants can shorten and simplify the process. The PVC formulator has available a variety of dispersed pigments in a number of vehicles and forms, including pastes in plasticizers, chips, powders, and pellets. In addition, the dispersion supplier may be expected to provide quality control information leading to standardization of shade and strength.

Pigments are manufactured to optimum particle size for color value, tinting strength, and transparency or opacity characteristics. Useful particle size ranges from about 20 nm with certain carbon blacks to micrometer (micron) size for iron, chrome, and other oxides. The opacity of a pigment depends directly on its refractive index, but inversely, up to a point, on its particle size. The refractive index of titanium dioxide, the highest of common colorless (white) substances, leads to its excellent opacifying characteristics. When the particle size of a pigment is reduced below one-half the wavelength of incident light, its ability to scatter light is largely eliminated. This point can vary somewhat with crystal structure, particle shape, and refractive index; it is of the order of 0.2 nm for titanium dioxide. This has become significant with the development of nanoparticle (submicron) titanium dioxide, having a particle size so small that light is not scattered or absorbed to any extent, resulting in transparency. Because of its high dielectric constant, it remains an excellent UV light absorber and is the basis for sunblock preparations. Although much more expensive than ordinary grades of titanium dioxide, it is beginning to find use in UV light-resistant clear compounds.

The capacity for color, transparency or opacity, and tinting strength of a pigment is, as a first approximation, independent of the formulation (excluding solubility considerations). Other properties affecting pigment suitability, such as heat stability, are affected by the choice of the other ingredients, or may influence this choice. Consequently, pigment evaluation requires a control formulation, without pigment, or with a similar pigment, as a reference standard.

Heat Stability The colorant is incorporated into a compound and subjected to static or dynamic heat aging at temperatures lower than would be used to evaluate the effects of heat stabilizers (in short-term tests). It is compared with a similar compound, without the colorant, that has been similarly aged. Pigments that fade or change color as compared with the control indicate a lack of inherent heat stability, or heat plus shear stability in the case of dynamic aging. Evidence of lack of stability lies in shift of the L, a, and b components of ΔE in a pattern different from that obtained from heat aging with no pigment, or in intensification of the color shifts found in the control samples. Often, red iron oxides are found to be shear-sensitive in compounds containing abrasive fillers.

Color shifts from chemical reactions are typically predictable and avoidable. There is, for example, every reason to expect a color shift if a pigment based on a metal that forms a dark sulfide, such as lead chromate, is used with a tin mercaptide stabilizer or thiodipropionate costabilizer.

Light Stability The light stability of a pigment may vary when used at sufficient levels for full color expression (referred to as "mass tone") or when used at low levels to obtain colors referred to as "tinted shades." Exposure to accelerated aging in weathering devices, such as a xenon arc (per ASTM G26) or fluorescent light cabinet (per ASTM G35), is typically used. Interpretation is similar to evaluating heat stability. Loss of color indicates lack of inherent light fastness. Premature discoloration, as compared with controls, indicates undesirable lack of stability. Light aging may cause migration of pigment to the surface, known as "chalking." This results from partial crosslinking of resin at the surface from oxidative degradation, increasing the modulus of the surface layer, and decreasing pigment compatibility. Pigments of high specific gravity, such as titanium dioxide, are particularly prone to chalking. Colors that are achieved with blends of titanium dioxide with other pigments may appear to lighten in shade as the former "chalks."

Sulfide Staining The pigmented compound is exposed to an atmosphere rich in hydrogen sulfide fumes per ASTM D1712. Note that, because of the toxicity of hydrogen sulfide, this procedure should be carried out only by trained personnel and with total compliance to the ASTM method. The change in color (usually significant darkening) indicates sensitivity to airborne sulfides, often present in industrial fumes. Because lead-based stabilizers and certain other additives will cause darkening, an unpigmented compound of the same formulation should be used as a control.

Migration (Bleeding, Blooming) In procedures basically that of ASTM D279, a sheet or film of the formulation is placed in contact with a similar white or uncolored sheet under a weight of 1 lb/in^2 (70 g/cm^2), usually for 5 hours at 180 °F (82 °C). Transfer of color to the uncolored sheet indicates migration (generally termed "bleeding"). Pigments that migrate will usually also "bloom" (appear on the surface of the article as a fine powder) after a period of storage at room temperature. Pigments that are slightly soluble in liquid ingredients such as plasticizers may bloom, and those that sublime may also bloom regardless of the presence of plasticizers.

Crocking This is a jargon term for tendency for color to rub off onto other objects. The testing procedures used are based on those specified for textiles by the American Association of Textile Colorists and Chemists (AATCC, www.aatcc.org) Test Methods 8 and 116. A piece of white, unsized fabric is rubbed across the plastic surface under constant pressure. After the specified number of rubs, the fabric is examined visually or colorimetrically for color pickup. The equipment is referred to as a Crockmeter. With flexible PVC articles, it is also possible to adapt the procedure of ASTM D5053, originally designed for use with leather.

Ease of Incorporation Evaluating pigment incorporation should be consistent with the methods of processing used in manufacture. A useful laboratory test involves banding a standard white compound on a two-roll mill. The pigment or dispersion to be tested is added and milled for 3 minutes. The batch is then removed, allowed to cool to room temperature, placed back on the mill and examined for color streaks and other evidence of unincorporated pigment. With compounds that do not mill well, the color dispersion should be added using a laboratory extruder under conditions comparable to plant operation.

Electrical Characteristics Wire insulations are usually colored using dispersions from suppliers specializing in materials for electrical applications. These are selected to have only minor effects on electrical properties; that is, to contain no more than traces of water soluble species. It is possible to purchase dispersions of the common wire and cable colors (red, green, and black) such that the ratio of dispersion to compound may be held constant in switching from one color to another, eliminating adjustments to the color proportioning equipment. These are referred to as “constant-volume, constant-SIC” color concentrates. (SIC, Specific Inductive Capacitance is the wire industry jargon for dielectric constant, a property of the insulation also sometimes called “relative permittivity.” It is a measure of the extent to which electrical energy passing through the conductor will induce a capacitative charge in the insulation; low numbers are desirable.)

Plateout This jargon term refers to the tendency of an additive to deposit on the surface of processing equipment. A colored compound is placed on a two-roll mill for at least 5 minutes. This is followed immediately with a white compound. The extent of color imparted to the white sheet by pigment left on the rolls is then determined. Pigments showing high plateout should be replaced. Often, changes in lubricant type and level are helpful in marginal cases. Plateout can also be reduced or eliminated by addition of absorptive fillers such as silica, zeolite, and alumina trihydrate (ATH). In addition, heat stabilizers can be formulated to inhibit or reduce plateout.

Resistance to Acid, Alkali, or Soap In the past, two or three drops of the test solution were placed on the surface of the pigmented compound for periods up to 3 hours. The compound was then washed, and the exposed spot examined for change in color. Samples are now tested by immersion per ASTM D5260.

The designation "toner" refers to pigments that are almost 100 percent active colorant. "Lakes" are pigments prepared in the presence of an inert extender of low refractive index, such as ATH or barium sulfate. The most common of these extended pigments are 60 percent color pigment and 40 percent extender, or the reverse. They have advantages in ease of dispersion, improved rheology, and less sensitivity to weighing errors. They are commonly used with more expensive pigments such as vat oranges, vat yellows, and vat blue. FD&C pigments are prepared by precipitating the approved FD&C colorant on such an extender (usually ATH). The characteristics of extenders are such that they have only a minor effect on the perceived color.

5.3 INORGANIC PIGMENTS

Many of the most durable pigments are metal oxides. Because they are relatively unreactive, properties such as heat stability and light stability, chemical inertness, and bleeding and other forms of migration, are usually good. These properties are often improved by calcining to remove impurities.

5.3.1 Titanium Dioxide

Titanium dioxide has two commercially important crystal forms: anatase and rutile. Both are tetragonal in an octahedral pattern. In anatase, the octahedra are packed so that four of the twelve edges of each octahedron are shared with adjacent octahedra; in rutile, two such edges are shared. Rutile has the higher refractive index (2.71) and abrasive index (6–6.5 Mohs hardness) and is more resistant to chalking than anatase. Anatase pigments generally have a slightly bluer shade; they are slightly lower in refractive index (2.55) and abrasive index (5.5–6 Mohs hardness) and are often easier to disperse. Surface treatments may consist of zinc oxide, aluminum oxide, silicon dioxide, or other oxides deposited in monomolecular layers by vapor-phase calcination. In many instances, these surface treatments can affect heat and light stability. Titanium dioxides, because of their excellent tinting strength and very high opacity, are the whitest pigments known. Older white pigments such as zinc sulfide, basic lead carbonate, and lithopone are far less common. Titanium dioxide is the most common pigment used in PVC by far. Anatase is produced from ilmenite ore by solution in sulfuric acid and hydrolysis (the "sulfate" process). Rutile is refined from rutile ore both by the sulfate process and, to higher levels of purity, by conversion to $TiCl_4$, distillation, and hydrolysis (the "chloride" process). A third crystalline form, brookite (orthorhombic rather than tetragonal), has recently been commercialized by Showa Denko under the trade name NTB®. It is a submicron photocatalyst and may possibly find use in PVC.

Most of the usage is of rutile, because of its superior tinting strength, opacity, and value in weatherability as a UV light absorber. These properties stem from its high dielectric constant (as with carbon black, too high for precise measurement). Anatase is commonly used in printing inks, food, pharmaceuticals, cosmetics, and rubber compounds. Commercial grades used in plastics have particle sizes below

0.2 μm, and therefore a strong blue undertone. If there is no weathering requirement, it can be used in PVC; for example, with black colorants to obtain gray shades, as in electrical conduit and cable jackets. Suitable anatase grades to consider include Millennium Tiona® AT-1 and Huntsman-Tioxide APP-2. Unless the usage is large, there is often no point in stocking anatase if rutile grades are also used. On the other hand, if weatherability and light resistance are not of concern, the lower abrasivity of anatase is very desirable, since it causes less equipment wear. Commercial grades for plastics, such as those cited above, have organic surface treatments to improve compatibility and reduce wear to processing equipment.

One of the most important uses of rutile is in the outer layer of vinyl siding, in window profiles, and related outdoor applications. Where nonchalking is desired, as in articles colored other than bright white (and some white applications as well), grades are used that have been surface modified with alumina and silica, leading to a highly inert surface. These include Tronox® 822 and 826 (Kerr McGee), TiPure® R960 (DuPont), Tiona® 696, TR-60 (Huntsman-Tioxide®), 2160 and 2220 (Kronos), and RS94 (3 N). Where chalking is desirable (some bright white outer layers) or of not much concern (pipes and outdoor substrates), the surface treatment is usually alumina. Available grades include Tronox® CR-834, TiPure® R102, Tiona® RCL-4 and RCL-6, Kronos 2200 and 2073, Kemira 660, and Tioxide® R-TC30. Grades recommended for lead-stabilized PVC for outdoor use include Tronox® R-FK-3, 3 N RP92, and TiPure® R103. Grades specifically recommended for flexible vinyl, including plastisols, include Tiona® RCL-4, Tioxide® TR23, TiPure® R102 and R104, Kronos 2210, and Kemira 405.

Although uncoated grades are available (e.g., TiPure® R960), most rutile pigments are surface-treated with organic coatings to improve speed of incorporation and reduce equipment wear. The grades suggested above for use in substrates and in flexible compounds typically have a blue undertone and have average particle size in the range of 0.15–0.20 μm. Nonchalking grades typically have a slightly brown undertone and have average particle size in the range of 0.2–0.25 μm.

5.3.2 Metal Oxide Pigments

At one time, pigments based on iron oxide were known for great stability but poor tinting strength. The trend towards elimination of the use of compounds of lead, cadmium, and mercury has driven the development of improved iron oxide pigments and of new mixed oxide pigments that cover a wide range of colors.

The oxides of iron vary from light yellow, red, to dark brown and black. The ores often contain metal impurities that may cause problems in use. When the ores are calcined, they are converted to their oxides and are unreactive at ordinary processing temperatures. Grades with sufficient heat stability for use in PVC include Mapico® 10A Tan, 806 Black, and 1000HRA Yellow (Rockwood Pigments); and Bayferrox® 30 and 3950 Yellow, 303T Black, 645T Brown, and 120M Red (Lanxess Bayferrox). A related product is Bayferrox GN-M Chrome Oxide Green. The products are also supplied by Impex Colors, who list them under their CI designations: Chrome Oxide Green–Green 17, Chrome Oxide Yellow–Yellow 34, Yellow

Iron Oxide–Yellow 42, Blue Iron Oxide–Blue 27, Chrome Oxide Orange–Orange 21, Red Iron Oxide–Red 101, Chrome Oxide Red–Red 104, and Black Iron Oxide–Black 11.

Recent developments have resulted in mixed oxide pigments with good tinting strength as well as thermal and light stability. For example, a broad range of useful pigments is now available from BASF under the trade name Sicopal®. These are mixed oxides with a highly heat-resistant spinel structure. They include K1160 (CI 184) Yellow (Bi/V-based); K2595 (CI 119) Brown (Fe/Zn); K2795 (CI 29) Brown (Fe/Cr); K6210 and 6310 (CI 28) Blue (Co/Al); K6710, 7210, and 7310 (CI 36) Blue (Co/Al/Cr); K9610 and 9710 (CI 50) Green (Co/Ti/Ni/Zn); and 0090 (CI 27) Black (Co/Fe/Mn/Cr).

Functionally similar pigments available from Heubach include CI Yellow 24 (various grades of Cr/Sb/Ti pigments under the trade name Heucodor® Yellow); CI Yellow 53 (grades of Ni/Sb/Ti, also designated Heucodor® Yellow); CI Blue 28 (Co/Al), Blue 36 (Co/Cr/Al), and Blue 50 (Co/Ti), all Heucodor® Blue; CI Brown 29 (Fe/Cr); and CI Black 28 (Cu/Cr) and Black 27 (Co/Cr).

Another broad range is available from Ferro under the trade name Geode®. They include CI Yellow 53, based on Ni/Sb/Ti (Geode® V-9412, 9415, 9416); Yellow 161 Ni/Nb/Ti (V-9440); Yellow 162, Cr/Nb/Ti (V-12107); Blue 28, Co/Al (V-9236 and V-9250); Blue 36, Co/Cr/Al (F-5686 and V-9248); Green 50, Co/Ti/Ni/Zn (V-11633); Green 26, Co/Cr (V-12600, V-12604); Brown 33, Zn/Fe/Cr (10363); Brown 24, Cr/Sb/Ti (10411, 10415); Black 26, Fe/Mn/Cu (F-6331-2); Black 28, Cu/Cr (V-7709); and Violet 14, Co/P (V-8291). A number of these have high solar reflectance and are pointed at vinyl siding and roofing applications. Specifically mentioned are Yellows (CI 53) V-9415 and V-9416, with solar reflectance (SR) of 67 percent; Yellow–Browns (CI 24) 10411 and 10415 (SR about 60 percent); Greens (CI 17) 10241 (SR 40 percent) and (CI 26) V-12600 (SR 28 percent); and Blues (CI 28) V-9248 and 9250 (SR about 30 percent). Specialty grades with unusually high reflectance include V-13810 Red and V-12650 Green, both with SR about 40 percent.

Other sources of high-solar-reflectance pigments include the Engelhard Meteor® series and the Shepherd Color Arctic® pigments Yellow 10C112 (CI 53), Green 10G663 (CI 50), Blue 10K525 (CI 28), and Brown 10P857 (CI 33).

The mixed oxide grades are used in combination with titanium dioxide in rigid vinyl siding, window profiles, outdoor furniture, fencing, and related products to achieve other than white products. Each compound using titanium/mixed metal oxide combinations must be checked for heat stability and outdoor weatherability. The levels of each should be chosen so as to provide margin of error. For example, if a white compound has been successful in the field using 9 phr of titanium dioxide, and it is desired to add a brown variant in which the desired color is given by a 2 : 1 blend of titanium dioxide and a brown oxide pigment, 6 phr of the first and 3 phr of the latter should be evaluated as a starting point. It is likely that 8 plus 4 will yield better performance. In some cases, it may be found that 5 plus 2.5 is adequate. Each shade, at least at first, becomes a development project.

In flexible vinyl compounds, combinations of metal oxide and organic pigments are often used. The latter typically adds a more intense, lustrous appearance. With natural aging, particularly outdoors, fading of the organic pigment leaves the oxide base color instead of the total color fading. This approach has been used for many years in garden hose covers.

Inorganic pigments that should now be avoided because of metal toxicity include cadmium sulfoselenide (CI Red 108 and Orange 20), cadmium mercury reds and oranges (CI Red 23 and 113), cadmium sulfide (CI Yellow 37), lead chromate (CI Yellow 34), and lead molybdate-based pigments (Molybdate Orange).

A common feature of inorganic pigments having good heat and light resistance is that they are difficult to oxidize. The metals present are in oxidation states, or suitably coordinated, so that one-electron oxidation, as might occur in resin degradation, does not proceed to yield changes in, or loss of, color. With judicious choice, they are also not catalytic with regard to polymer degradation.

5.3.3 Carbon Black

Carbon black has several uses in PVC. Its use to provide semiconducting or charge-dissipating properties is discussed in Section 6.5 Most carbon blacks are made by the furnace process, in which aromatic distillates are injected into burning gas in a closed reactor. Control of oxygen content, temperature, distillate type, and addition procedure leads to a range of products of different particle size and surface structure, and to reactive oxygenated surface groups. These features provide reinforcement and rheological properties of great value in the formulation of elastomers and elastomer/resin blends. Only a few grades are used as pigments in PVC.

An important use is as a UV light absorber. Carbon blacks are classified by particle size and structure per ASTM D3053. The type used most frequently for UV light absorption is N-110 SAF (Super Abrasion Furnace Black). Trade names include Vulcan® 9A32 (Cabot) and Raven® C (Columbian). This grade, originally developed for heavy duty tire tread, tank track, and railway pads, has a notably high UV absorption coefficient (500, per ASTM D3349). It is notoriously difficult to disperse, and should be added as a dispersion. Black compounds use 2–3 phr; gray, usually fractions of 1 phr with a normal titanium dioxide loading. Gray compounds are the most frequent application. With black compounds, it is more cost-effective to use 2–4 phr of N-330 High Abrasion Furnace Black (HAF) instead. This grade, used principally in tires, has a UV absorption coefficient 90 percent that of N-110, is of lower cost, and is more readily dispersed. Grades include Regal® 330 (Cabot), Raven® 1020 (Columbian), and Printex® 45 (Degussa).

For use simply as a colorant, the choice lies between a black metal oxide pigment and carbon black. If the highest jetness and luster is desired, certain black oxides make sense. If the object must merely be black or gray, and cost considerations are significant, carbon black is used. The grade most frequently used is N-660 General Purpose Furnace Black (GPF), the lowest-cost furnace black, used widely in EPDM roofing and similar articles. Grades include Regal® 660 (Cabot), Raven® 1200 (Columbian), and Printex® 55 (Degussa).

In practice, carbon blacks employed as colorants are almost always used in predispersed forms. This improves plant cleanliness and ease of dispersion in the compound, as well as enabling a neutral base compound to be colored during processing. A further advantage is that the dispersion process eliminates (or at least reduces) the traces of grit and metal particles found in general purpose carbon blacks.

Carbon black was also formerly made in North America by the channel process, which has been discontinued because of the levels of air pollution associated with manufacture. Certain grades are excellent pigments. Although available through importation, their use in PVC should be avoided, with the recognition of air pollution as a worldwide problem. Carbon black is also available from the thermal process—combustion of natural gas under conditions where hydrogen is oxidized and carbon deposited. The ASTM designation for the most common grade, Medium Thermal (MT) Black, is N-990. It is of large particle size compared with furnace black, and in PVC, at levels of 1–5 phr, yields gray and blue–gray colors. Since MT black is relatively nonconductive, it can be used to produce gray wire insulation or conduit. It provides, however, little or no UV light absorption.

5.3.4 Special Effect Pigments

Metal Flake Pigments Although many metallic elements are used in the paint, ceramic, and printing ink industries, PVC usage is limited to aluminum, colored aluminum, and occasionally copper, and bronze, all entirely in flexible compounds. The pigments are prepared by cutting foils or by hammering the metal into thin sheets with a lubricant such as stearic acid. When the latter is done, the product is said to be "leafing." This refers to the pronounced effect achieved when the flakes are oriented in a plane parallel to the surface, assisted by interaction of the lubricant coating. Reflectance is similar to the specular, or mirrorlike, reflectance from the metal itself. Using coarse flakes (approximately 200 mesh) and processing at slightly higher than normal temperatures will enhance the metallic effect. Flakes prepared by cutting unlubricated metal foil tend to distribute more randomly in the compound, have less of a specular effect, and are referred to as "nonleafing." Commonly articles containing more or less nonleafing flakes show differences in appearance when viewed at different angles. The jargon term for this effect is color "flop."

In PVC, copper and bronze flakes are used in molded plastisol fishing lures. It is widely thought that these colors are more effective than a silver appearance, particularly with fresh water bass. The color perception of fish is basically guesswork; it is likely that they distinguish color differences very differently than humans. Since copper is a prodegradant, copper and bronze pigments should be used only in applications where processing and service conditions are mild. Copper flake is available from Ferro in several size grades (Copper Flake 300, 550, and 800), from Unicore Canada (UCF 3, 5, and 8 μm), Amepox (AX 20 and 6–12 μm) and from MD Both (Premior® 10, 17 and 45 μm). Bronze flake is available from MD Both (Premior® Std, ExtraFine and Superfine, 45, 17, and 10 μm) and from BCA Marketing (US Bronze).

Aluminum flakes do not catalyze PVC degradation under normal processing conditions, and show only slight dulling on long-term exposure to light and humidity. On the other hand, finely divided aluminum is highly reactive—the basis for its use in pyrotechnics and propellants. Aluminum metal should not be combined with metal oxide pigments, particularly those of iron, because of the danger of initiating thermite-type exothermic reactions. It should also be used with great caution in latex formulations, since deviations from neutral pH can cause reaction with water, yielding hydrogen. Combinations of aluminum flake and pigments with oxidizing capability, such as chromates, should be avoided. Perhaps the best approach in flexible PVC compounding is to use aluminum flake coated with low-molecular-weight polyethylene wax. Such products are supplied by Silberline in both leafing and nonleafing grades of various particle size under the trade name Silvet®. These include reflective grades, Series 540 and 620; Series 760, 790, 880, and 960; Silvex® Series 838, 860, 890, and 950, pointed at automotive coatings; and glitter grades often used with other colorants, Series 410, 420, 430, 440, and 460. Guidelines for use are given in the Silberline publication *Aluminum Pigments for Plastics Applications*.

Other suppliers include Toyal America, with leafing grades ATA 2100 (32 μm), 5100 (18 μm), and 7100 (13 μm), and nonleafing grades ATA 2000 (36 μm) and 3100 (17 μm); and Transmet, with coarser rectangular (K-101) and square (K-102, K-109) flakes.

Many metallic colors and tones can be obtained by using transparent organic pigments in combination with aluminum flakes. Gold, copper, brass, and bronze colors of good lightfastness and heat stability can be prepared by using transparent yellows with or without red. The effect created is a yellow, gold, or bronze color distributed throughout a film. A metallic effect is also obtained by coating thin aluminum foil on both sides with a resin colored with transparent, durable, nonbleeding pigments. The coated foil is then cut into very small flakes. They are available in two grades: "glitter," from 0.005 to 0.010 in (0.13 to 0.25 mm) in diameter, and "flitter," from 0.015 to 0.100 in (0.38 to 2.54 mm) in diameter. Flitters and glitters can be incorporated into clear, colored, transparent, pastel, or white film to give unusual color effects. They are seldom used as the sole colorant of a film, but instead to give a speckled effect, especially in floor coverings. Such products are available from BASF under the trade name Variochrome®, including Gold K 14111, Red 4111, Green 9811, Silver 1000, and Purple 5511. Use at levels of 0.05–0.15 percent provides a semitransparent effect, while levels of 0.5–2 percent are used in opaque articles. With all flaked pigments, compounds must be tested (and often reformulated) for resistance to plateout.

Pearlescent Pigments Complex rainbow effects can be achieved through interference and reinforcement of reflected light by thin films on a reflective surface. This has led to pearlescent pigments based on metal oxide (often titanium plus iron) coatings on mica flakes. A range of colors is available from EMD (formerly E.M. Industries) under the trade name Iriodin®, and from Engelhard under the trade name Mearlin®. Other suppliers include Sun Chemical (SunShine®), Oxen Chemical (Polychrome®), Southwestern Pigments (Cres-Lite®), BASF (Sicopearls®), and Millennium. EMD also supplies a series based on alumina rather than mica (Xirallic®) and one based on silica (Colorstream®). Engelhard offers a range of colors based on borosilicate coated with iron and titanium oxides under the trade names Firemist® and Reflecks®. A pearlescent effect can also be obtained by combination of organic pigments with low levels (0.05–0.25 percent) of special purpose aluminum flakes, such as Silberline ET-2018 and ET-2271. Although these products were designed to make expensive items such as automobiles appear irresistible, there is no reason not to experiment with their use in more prosaic plasticized PVC applications, such as shower curtains, wall coverings and automotive upholstery.

Fluorescent Pigments This class covers pigments that fluoresce under UV light and under the near-UV end of natural light, adding brightness and vibrancy to the article. Their use in PVC is limited by low lightfastness in exterior applications and decomposition temperatures in the range of 200 °C. The major supplier is the Day-Glo Color division of RPM, Inc. In PVC, the VC and VR series of Day-Glo® pigments should be used. These cover a range of colors. Fluorescent dyes are available from BASF under the trade name Lumogen®; these include perylene yellow, orange, red, and green, and naphthylimide blue and violet. The dyes may be used in semirigid applications.

5.3.5 Ultramarine Blue

Ultramarine blue, sodium aluminum sulfosilicate, $Na_{8-10}Al_6Si_6O_{24}S_{2-4}$, was originally ground lapis lazuli, now mined chiefly in Afghanistan, but used as an artist's pigment for millennia. Although produced synthetically for two centuries, it is still occasionally referred to as *bleu outremer.* In the synthesis invented by Guimet, mixtures of kaolin clay, sodium carbonate, and sulfur are calcined. The nature of the chromophore is open to speculation. Kaolin typically contains 0.2–1.0 percent iron oxide and 0.2–0.5 percent titanium. The ultramarine pigments have a zeolite structure containing di- and trisulfide groups, which are not normally strong chromophores, but are possibly so if present as radical ions coordinated to trace iron and titanium.

Reddish blue (CI Blue 29), pink (CI Red 259), and violet (CI Violet 15) shades can be produced. CI Blue 29 has FDA sanction for indirect food contact, and is widely used in cosmetics (ASTM D262). Most manufacture has shifted away from North America and Western Europe. Suppliers include Mineral & Pigment Solutions Inc. (MPSI), formerly Whittaker, Clark and Daniels; Holiday Pigments, trade name Artizan®; Habich GmbH; Nubiola (Barcelona); and PD Industries and Ultramarine & Pigments Ltd of India.

Ultramarine blue is stable in processing to 250 °C, but is not highly lightfast outdoors. In PVC, it is important to use acid-resistant grades to avoid fading during processing. Standard grades are not acid-resistant. The major use is as a blue toner to counter yellowing. The formulator should investigate whether use instead of a phthalocyanine blue, or a judicious choice and level of organophosphite costabilizer might not be more suitable.

5.4 ORGANIC PIGMENTS

Blue The most common organic blue pigment used in PVC is phthalocyanine blue, CI 15. Typically, suppliers have acid-resistant grades for PVC. Examples include Clariant PV Fast® Blue A2R, BASF Heliogen® Blue K6850, Heubach PB15, and Ciba Irgalite® Blue NGL. There is occasional use instead of Indanthrone blue, CI 60, such as Ciba Chromophtal® Blue A3R and Heubach PB60. It has lower heat resistance than phthalo blue and should probably be restricted to use in plastisols. Both have reasonable weatherability, but in exterior applications should be backed up with an inorganic blue. Such a combination is actually useful in all filled applications, as it decreases the occurrence of metamerism. Blue-colored clear compounds almost always use phthalo blue.

Green Organic green pigments are also usually based on copper phthalocyanine compounds. Chlorinated phthalocyanine leads to CI 7, blue shade phthalo green, such as Clariant PV Fast® Green GNY, Heubach PG7, and BASF Heliogen® Green K8730. Bromination leads to yellow shade phthalo green, CI 36, as in BASF Heliogen® Green K9360 and Heubach PG36. In filled compounds, it is best to use these in combination with an inorganic green, using the organic pigment to increase color richness. Both blue and green phthalo pigments have relatively broad FDA sanction.

Violet The most common choice is perylene violet, CI 29, which has FDA sanction and reasonable heat and light resistance. An example is BASF Paliogen® Violet 5011. Other possibilities include dioxazine violet, CI 23, such as Ciba Chromophtal® Violet GT, again with reasonable heat and light resistance. Where heat resistance is less important, as with some plastisols, quinacridone violet, CI 19, such as Clariant PV Fast® Violet ER or Heubach PV19, could be used. Violet organic pigments are also used to modify an inorganic red or blue base color.

Brown The first choice is usually benzimidazolone brown, CI 25, such as PV Fast® Brown HFR. Heat resistance and light stability are better than with diarylide browns, CI 41, such as PV Fast® Brown RL.

Orange Benzimidazolone is again a good starting point, CI Orange 72, as in PV Fast® Brown H4GL, providing relatively good heat and light stability. Other grades include Heubach PO62. Weatherability is better than with diarylide orange, CI 13, such as Clariant Graphtol Orange GPS. Perinone Orange, CI 43, and CI 36 diarylide Orange could also be considered, as could isoindolinone, CI Orange 61.

Yellow Yellow pigments with superior heat and light resistance include benzimidazolone yellows, CI 151 (Clariant Hostaperm® Yellow H4G, Heubach PY151), CI 120 (PV Fast® H2G), 181 (PV Fast® H3R), and quinophthalone yellow CI 138, FDA-sanctioned, such as BASF Paliotol® K1090. If weatherability is not a factor, isoindoline yellow, CI 139 (Graphtol® H2R and Paliotol® K1841) and diarylide yellow, CI 81 (Graphtol® H10G) could be included.

Red Best choices include FDA-sanctioned perylene reds, CI 149 (PV Fast® Red B and Paliogen® Red K35880), CI 178 (Paliogen® Red K3911), and CI 179 (Paliogen® Red K4180). Another good option is benzimidazolone red, CI 208 (Graphtol® HF2B). If a pink or magenta color is desired, quinacridone red, CI 122 (Heubach PR122) and CI 202, is a reasonable choice. Where weatherability is not a factor, diarylide red, CI 144 and CI 214, and diarylide red CI 81 and isoindoline red CI 139 have sufficient heat stability for use in PVC. In plastisols, reds with lower heat stability such as pyrazolone red, CI 37 and 38, can be used.

A number of grades of organic pigments are also supplied by Engelhard and Sun Chemical Division of Dainippon. Large-scale distributors include Lenape Chemical.

Heat- and light-resistant organic pigments are typically large molecules with a number of aromatic or quinoid rings (four in the case of phthalocyanines, isoindolinones, and diarylides; five or more in quinacridones, dioxazines, anthroquinone dimers, perylenes, indanthrones, and benzimidazolones). The chromophore is large—not as large as with most inorganic pigments, but large compared to pigments that migrate or fade. These chromophores are relatively difficult to oxidize. In fact, many have hindered secondary amine groups that resemble antioxidant structures. As regards the polymer, antioxidant function is no doubt minimal, since the pigments are chosen for low mobility in the resin matrix. In terms of their own oxidation, however, it is reasonable to view them as stationary antioxidants.

5.5 OPTICAL BRIGHTENERS

Optical brighteners are organic molecules that absorb radiation in the near UV and re-emit in the visible range. The main commercial applications are in paper and fabric coating to enhance color brightness. They can be used in PVC with two restrictions: they do not persist indefinitely; that is, they are slowly oxidized. This tends to restrict usage to interior applications. Secondly, the presence of organic UV light absorbers interferes with their action. Therefore, in PVC, the main areas of application are in decorative films, commonly in label stock. Levels of 0.02–0.1 percent are used in clear tinted compounds; 0.1–0.5 percent in white or other opaque film or sheet. Two classes of brighteners are the most common: substituted stilbenes and benzoxazole derivatives. Suppliers include Ciba (Uvitex® OB), Eastman (Eastobrite® OB-1, OB-3), Clariant (Hostalux® and Leucophor®), Lanxess (Blankophor® and Phorwite®), BASF (Ultraphor), and Odyssey Chemical of Beijing. Large-scale distributors include Grant Industries (Calibrite) and Lenape

Chemical (Lenbrite). When used in combination with organic pigments, the possibility of interaction should be checked thoroughly.

5.6 GLOSS CONTROL AGENTS

The most satisfactory method for development of a satin, rather than high-gloss, finish in filled rigid vinyl is through choice of impact modifier. In extruded exterior products such as siding or profile, acrylic impact modifiers can be selected so as to achieve the desired finish. Useful products are available from Arkema (Durastrength®), Rohm & Haas (Paraloid®), and others. Their effect is to generate microscopic protrusions from the surface that scatter light. Special products in these series have been developed for use with wood fiber composites and in clear rigid compounds; manufacturers should be consulted for the latest recommendations. Other methods of reducing gloss in rigid vinyl, such as adjustment of extrusion die temperature or embossing, tend to lower impact strength. If impact strength is not a concern, ultrafine polymer particles that are not impact modifiers can be used, such as acrylics (Reichhold Fine-Clad®) or polyamides (Arkema Orgasol®), for gloss control.

In flexible vinyl compounds, gloss is usually controlled with 1–3 phr of fine particle silica or talc, occasionally with ceramic microspheres. Measured gloss (ASTM D523) is, however, often lower in plasticized compounds if 2–5 percent acrylic impact modifier is used instead. This approach provides lower haze, generally better physical properties, and reduced equipment wear. The use of fine-particle fillers is preferable in cases where it is also operating to reduce plateout.

CHAPTER 6

Fillers and Reinforcements for PVC

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6.1 MINERALS FOR FILLERS AND REINFORCEMENTS

Mineral fillers are naturally occurring or synthetic nonblack, nonmetallic solid-surface particles. Such fillers have assorted shapes, from nodular to platy to acicular. When describing filler shape, the term “aspect ratio” is employed to describe the relationship of one dimension to another. Mineral fillers for PVC have historically included calcium carbonate (ground and precipitated), alumina trihydrate (ATH), barytes, talc, mica, kaolin, feldspar and nepheline syenite, and wollastonite.

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Property improvements such as mechanical strength, flame retardance and weight have been key contributions. For industries such as wire and cable, electrical properties also become very important.

Typically, mineral fillers have been exhaustively described along with their effects. Because mineral fillers can contribute more than just cost reduction, the industry has often used the term "functional filler" to signify their added importance. For instance, a function of selected fillers could be to improve tensile strength and elongation. Some fillers can improve hardness, while others improve heat and electrical resistance. Stiffness is often a sought-after property that can be improved by functional fillers. Fillers that are used mainly to reduce material costs are often referred to as diluents. Nevertheless, such fillers, even if not improving physical properties, often add to ease of processing and product acceptability, such as by reducing plateout, blocking and roll sticking, controlling gloss, improving UV light resistance and extrudability, and decreasing dry blending time. Thus, in a sense, all fillers are "functional."

Rigidity (stiffness) is a key property of PVC compounds; measurement of this often is reported as flexural modulus. Optimizing this property, as opposed to tensile modulus, maximizes the effect of the aspect ratio of the filler. For example, loadings of calcium carbonate, a low-aspect filler, provide only a small increase in rigidity in PVC, with little difference being found between precipitated (PCC) and ground (GCC). To raise flexural modulus in a typical compound by 30 percent, addition of about 60 percent of GCC or PCC would be required, to some extent affected by particle size, since the modulus of the compound increases as average particle size decreases. Fillers having higher aspect ratio, such as talc, are more effective in increasing rigidity. Ideally, a balance of stiffness and impact resistance is desired. It is generally thought that there is a critical particle size for fillers to obtain an optimum balance of these properties in PVC compounds, at about 1 μm.

In the building industry, dimensional stability is very important; thus, the coefficient of thermal expansion is measured. The value is greatly influenced by the aspect ratio of the filler. High values increase overall stress in the finished product and can lead to distortion or, in constrained articles, to cracking or buckling. At normal loadings, calcium carbonate provides a minor increase in dimensional stability. A filler of higher aspect ratio, such as talc, provides further improvement, particularly at higher temperatures. In the aspect ratio extreme, use of glass fiber, for example at a 15 percent loading, provides a major reduction in thermal expansion. This is not to say that such substitutions are immediately practicable. Nevertheless, the formulator should appreciate that such options are possible and could be implemented if needed.

Plasticized PVC, being essentially amorphous, can accommodate fillers of a variety of shape and composition. High-aspect-ratio fillers tend to have strongly negative effects on the impact resistance of unplasticized PVC, their sharp edges leading to crack propagation and decreasing the remedial effects of crazing and shear banding (Chapter 10). This underlies the prevalence of low-aspect-ratio calcium carbonate. Blends of calcium carbonate with high-aspect-ratio fillers often improve impact resistance compared with the latter used alone. The most effective remedy, however, is the use of polymeric impact modifiers to defeat crack propagation. Impact modification by means of a combination of filler and impact modifier particles is currently under active study.

6.2 CALCIUM CARBONATE

To many vinyl technologists, “filler” means calcium carbonate. The overall balance of properties gained and its low cost have led to usage in most rigid and flexible products other than in clear articles. Most grades of calcium carbonate come from the mineral calcite and are denoted by the terms “ground limestone” and “whiting.” The mineral chalk, microcrystalline calcite, is occasionally a source. In addition, there are many grades of synthetic precipitated calcium carbonate, typically more expensive, but often providing more functionality.

Naturally occurring calcite contains 93–98+ percent calcium carbonate. The major impurity is magnesium carbonate, 0.5–5 percent. When this impurity is high, the product is commonly referred to as “dolomitic” calcium carbonate, from the mineral dolomite, with a ratio of 54.3 percent calcium, 45.7 percent magnesium carbonate. Dolomite is slightly harder than calcite (Mohs hardness of 3.5–4 versus 3) and is more insoluble in water and dilute acid, but is generally thought harder to disperse. Dolomitic calcium carbonate is often used in flooring components, since it tends to be of lower cost than grades with low magnesium carbonate.

Other impurities of interest are silica and silicates; these range from 0.1 to 1.5 percent. This is the fraction responsible for abrasive wear of equipment. Grades with the highest levels are typically those of lowest cost. Appropriate remedies (see Section 6.3) include mixing techniques that minimize shear-driven abrasion and hardened equipment surfaces. Another impurity of interest is iron oxide, a prodegradant, present at levels of 0.01–0.15 percent. When grades with iron in the higher range are used, its effect (and that of other transition metal oxidation catalysts) can be minimized by inclusion of a scavenger such as zeolite or hydrotalcite in the stabilizer system. High iron levels also add color to the filler, as does traces of carbon found in some grades.

6.2.1 Properties of Calcium Carbonate

Calcium carbonate particles are nodular, with low aspect ratio. Ground calcium carbonate (GCC) is produced by both dry and wet processes. Dry-ground calcium carbonate particles are very irregular, with a broad size distribution and rough surfaces. Water-ground calcium carbonate has a narrower distribution and smoother surface, with fewer fines, better packing, provides greater viscosity stability in plastisols and coatings, and has a lower tendency to fracture. It is, of course, more expensive. Precipitated grades (PCC) are far smaller, more uniform, more functional, and more costly.

With nodular fillers, size is commonly described in terms of equivalent spherical diameter (ESD), the diameter of a sphere having the same volume as the particle. With ESD of 40 μm or less, particle size distribution is usually determined by sedimentation methods. The familiar curves produced graph the weight percent of the particles versus ESD. Such graphs are produced automatically by instruments such as the SediGraph® (Micrometrics Instruments). Commonly the mean particle size, that of 50 weight percent, is reported as the "average" particle size. Formulators should, however, examine the entire particle size distribution curve, particularly for indication of excess fines and unduly large particles. Large particles may disperse poorly, affecting appearance and compromising electrical properties. Excess fines often impede incorporation and affect compound viscosity.

Particle size in coarser fillers is often reported in terms of screen analysis. Filler mesh size is the finest screen that allows a given percentage (98, 99, 99.5 percent, etc.) to pass through the screen of that mesh, either by dry or wet screening methods. Many fillers, particularly if dry-ground and air-classified, have such small fractions of large particles as not to be evident in sedimentation curves. Thus, it is possible to have a test sample showing no particles greater than 20 μm via sedimentation, but nevertheless find a small number of particles retained on a 325-mesh (44 μm) screen. Such particles may not only cause surface roughness, but, in some cases, also exceed product thickness. In addition, silica and silicate content in such large particles will cause much greater abrasive wear. Even low concentrations can negatively affect impact resistance. It is therefore important to the formulator to know exactly what he or she is dealing with, so as to select the most appropriate grade and to compensate for any side issues.

Packing fraction (PF) is the volume fraction of filler at which point all of the interstices between filler particles have been filled with the polymer matrix, creating a composition that is essentially a block of polymer-treated filler, rather than a readily processed compound. For customary processing, compositions must be formulated with filler loading lower than the PF. Packing fraction data from suppliers is usually derived from *ad hoc* experiments based on the extent to which a filler can absorb a test oil, representing the polymer, and retain some measure of flow, or, with less than high precision, using ASTM methods D 241 or D 1483. The vinyl formulator is more likely to assess the effects on processing of increased filler loading by measuring compound viscosity in a capillary or torque rheometer, and the effects on properties by comparing with control samples. The packing fraction of calcium carbonate is notably increased by surface coating with stearic acid or calcium stearate (usually about 1 percent by weight) enabling high filler loading at a given process viscosity.

Although the starting limestone ore may have some porosity, once ground, the filler particles are too small to have significant pore structure. Particle facets are smoother with wet- than with dry-ground products. Precipitated grades have uniform rhombohedral shapes, with smooth facet surfaces. Surface area is lower than that of silicate fillers of comparable ESD. The specific gravity of various grades of calcium carbonate reflects the ratio of dolomite (2.85) to calcite (2.71). Precipitated grades can have higher values because of the formation of calcium carbonate in the crystalline form of aragonite (2.95) instead of calcite. The refractive index of calcium carbonate is about 1.65. This is not sufficiently higher than that of PVC (1.55) and of most plasticizers to provide high opacity. Thus, when an opaque stabilizer, such as tribasic lead sulfate, is replaced with calcium and zinc carboxylates, typically titanium dioxide (refractive index of 2.76) is added to provide equivalent opacity. (Neither zeolite nor hydrotalcite acid scavengers lend appreciable opacity at the levels at which they are used.)

In applications where color value is important, the formulator should choose grades of calcium carbonate with the highest brightness, such as 90 percent, the reference being the reflectance of a magnesium oxide surface. This will minimize the pigment levels needed—usually a cost-effective measure compared to the savings found by using lower-brightness grades of filler. Calcium carbonate with a brightness value of 92 or higher will add opacity and maximize color value.

When corrected for their high density (i.e., taken on a volume basis), mineral fillers have little effect on the thermal conductivity or specific heat of vinyl compositions. With most solids, electrical and thermal conductivity are linearly related. Electrical-grade fillers such as calcined clay, however, do not notably affect thermal conductivity. This reflects their mechanistic action in interfering with electrical conduction; if the insulator behaved electrically as a weighted average of PVC and clay, it would offer no benefit over calcium carbonate. A thermal property of greater significance is the coefficient of expansion. Mineral fillers are about two orders of magnitude lower in coefficient of thermal expansion than vinyl. Dimensional stability is an important property in articles such as flooring, where expansion cannot normally be accommodated by engineering design (as with vinyl siding). Thus, the high levels of filler used are necessary for service—not solely diluents to lower material cost.

Surface treatment most often uses stearic acid, typically applied as the molten liquid (the most common form in large-scale usage) at about 70 °C, at which point reaction with the filler surface occurs, yielding water, carbon dioxide, and a surface layer of calcium stearate. The water of reaction can be removed by application of vacuum or, less conveniently, by increasing the reaction temperature to 100 °C or more. In some cases, it may be more convenient or cost effective instead to blend the filler with about 1 percent calcium stearate, usually an "overbased" grade, having an excess of calcium, with Ca—OH groups present. Again, at about 70 °C, exchange and complexing occurs, yielding a stearated particle surface. With both procedures, the product is generally sufficiently hydrophobic to float on a pure water surface. This can be used to gauge the extent of treatment (QC determination of the fraction that sinks in a given time with a reference fluid of standard surface tension).

Precipitated calcium carbonate is treated prior to precipitation with sodium stearate, generating a calcium carbonate–stearate precipitate. Since stearate groups are not compatible with the calcite (or aragonite) crystal, they appear at the particle surface.

There is very little use of other surface treatments with calcium carbonate, largely because the surface does not provide reactive sites for coupling agents. If the formulator wished to experiment with coupling agents in calcium carbonate filled PVC, a starting point would be to treat an uncoated grade with, for example, hydroxystearic acid, providing a reaction site for an amino- or mercaptosilane.

6.2.2 Processing of Calcium Carbonate/PVC Compositions

When calcium carbonate is stearate-treated, its hydrophobic surface is easily wetted by the polymer matrix, leading to rapid incorporation. Untreated calcium carbonate has a hydrophilic surface as a result of adsorbed moisture, which is harder to wet. In addition, the polar nature of the surface leads to particle agglomeration, requiring work input to achieve dispersion, the breakup of agglomerates. Both incorporation and dispersion are accomplished by a combination of heat and shear in a high-intensity mixer: shear causing breakup of agglomerates, and heat leading to removal by evaporation of surface water and increase in polymer chain mobility. The length of time for which shear is applied at a given temperature is very significant. One cannot, for example, double the shear rate and expect incorporation and dispersion in half the time. With a high-molecular-weight, non-Newtonian fluid such as the typical polymer, the relationship is complex. (In low-molecular-weight analogs, such as low-molecular-weight PE, it is possible to achieve very rapid incorporation with extremely high-shear input, as long as flow is sufficiently streamlined to avoid cavitation.)

The calcium carbonate surface, irrespective of treatment, retains Ca—OH groups, leading to alkaline pH. As a result, the filler serves as a secondary stabilizer, providing greater heat stability than a clear formulation with otherwise comparable ingredients. Mixed metal stabilizers, lubricants, lubricating processing aids, and lubricating organotin stabilizers all tend to promote calcium carbonate dispersion. The 0.2–0.3 parts per 100 of resin (phr) of stearic acid found ubiquitously in PVC formulations often function primarily as a filler dispersant. In order to forestall adsorption of components of the stabilizer system, such as metal carboxylates, on the filler surface, the best course is to use calcium carbonate that has been pretreated. This is typically cost-effective as opposed to increasing the level of stabilizer. One cannot expect, however, to compensate for inadequate stabilizer efficiency or level with high loadings of filler. Highly filled compounds instead usually require an increased level of stabilizer to compensate for the decrease in additive mobility as filler level is increased.

Surface treatment also lowers abrasion of equipment by fillers. Although particles with Mohs hardness below 5.5 do not scratch steel in experimental tests, under actual high-shear mixing conditions, they accelerate loss of steel through wear. (Aluminum surfaces have about the same hardness as calcium carbonate, and should be avoided.) Wear is costly not only in terms of equipment reconditioning or replacement, but also because metal contamination reduces heat and service stability of vinyl compositions and affects appearance. Typically, the latter effect is noticed only after significant wear occurs. The presence of contaminant particles in calcium carbonate, particularly in dry-ground products, greatly increases abrasiveness. The fraction of acid-insoluble material in calcium carbonate ranges from less than 0.1 percent in some precipitated grades to several percent in coarse dry ground products. Such insoluble particles are commonly silica and silicates. It should be noted that minor fractions of titanium dioxide (Mohs hardness 7.5), often a necessary ingredient, notably increase filler abrasiveness. Calcium carbonate insolubles may be determined readily by reaction with dilute hydrochloric acid, filtration and drying. Sharp-edged abrasive particles are clear at 100× magnification.

The viscosity of a plastisol in which filler is dispersed, η, is related to that of the unfilled plastisol, η_0, and the product of the volume fraction of filler, V_f, and the Einstein coefficient, k_E:

$$\eta = \eta_0(1 + k_E V_f)$$

In this, a form of the Mooney equation, the Einstein coefficient describes the shape of the particles, 2.5 denoting a sphere. Dispersion resin particles are in the range of 2.8–3 and calcium carbonate 3–4. In this relation, η_0 refers to the viscosity of the unfilled plastisol under the same shear conditions as η, which is obviously an approximation. It can be seen that the effect of the Einstein coefficient is that any significant loading of filler will have very substantial effects on plastisol viscosity, and that the greater the aspect ratio, the greater the effect. This, of course, can be turned to good effect by use of high-aspect fillers to adjust plastisol viscosity upward to a desired level for processing.

In practice, plastisol viscosity is evaluated using a Brookfield viscometer or similar equipment, whose output is apparent rather than true viscosity; that is, it is highly dependent on the configuration of the measuring device. The measurements, however, provide useful comparisons of one formulation to another, keeping in mind that the shear rates involved in measurement may be rather different than those in actual processing. It is entirely possible for viscosity versus shear rate curves to cross at sufficient difference in the latter. That being said, it is usually possible to predict processing behavior from measurements of apparent viscosity. In general, apparent viscosity at constant filler loading increases with decreasing particle size of the filler and decreases with use of surface treatments. Apparent viscosity may also increase as a result of poorly dispersed filler agglomerates trapping plasticizer, which is then less available to promote flow. It is therefore a common QC measurement.

In applications other than plastisols, melt viscosity is routinely determined using a capillary or a torque rheometer. The former uses a configuration of geometry simple enough that true viscosity can be obtained and covers a wide range of shear rate. As normally used, the torque rheometer provides apparent viscosity over a narrower range of shear rate, but one that is generally appropriate to mixing and extruding. Processes with very high shear rates, such as injection, are best simulated with a capillary rheometer. Surface treatment of calcium carbonate typically lowers melt viscosity. In extrusion, in both rigid and flexible PVC, it is generally found that filler acts to increase frictional heating, speeding fusion and increasing output.

6.2.3 Properties of Calcium Carbonate-Filled Compositions

Calcium carbonate of fine particle size ($<1–2$ μm) will increase the tensile strength of PVC modestly up to about 20 phr loading, after which it drops steadily. This is true of both rigid and flexible PVC at typical plasticizer levels. The effect is probably a combination of true reinforcement (van der Waals attraction to polymer chains) and plasticizer adsorption by fine particles. With soft, highly plasticized compounds, the reinforcing effect may be too small to notice. Coarse-particle-size calcium carbonate causes a steady drop in tensile strength in all compounds as the level is increased.

At relatively low plasticizer levels, up to 20 phr of fine-particle calcium carbonate, particularly surface-treated grades, can actually provide a minor increase in ultimate elongation. As the plasticizer level is increased, this effect disappears, but elongation may remain steady at 10–20 phr filler loading. Coarse-particle-size calcium carbonate causes a continuous decrease in elongation with increasing loading, approaching zero as the PF is approached.

The above effects on tensile strength and ultimate elongation are increased by substitution of fillers of higher aspect ratio for calcium carbonate. Properties at failure may be convenient for QC testing, but only indirectly reflect fitness for service, where (one hopes) tensile failure will never be reached. Performance would be better assessed by accelerated tests involving increasing the frequency of deformation and stress rather than intensity; that is, by dynamic mechanical analysis (DMA). Such experiments with PVC compositions are, to date, rare, making this a fascinating field for the technologist.

The properties of interest during service are modulus at low strain and impact resistance. Low-elongation modulus is relatively flat, with increasing loading of calcium carbonate of all types (up to a point—often that at which decreasing elongation makes the measurement at, for example, 100 percent elongation, impossible). With DMA, this could be studied in tensile or compression modes at strains thought to be encountered in service. Modulus affects compound hardness, but is not the only factor. Typically, hardness increases linearly with calcium carbonate loading up to a point.

In compounds where calcium carbonate provides a slight reinforcement of tensile strength (i.e., low loadings of a fine particle grade), there is likely to be a corresponding improvement in tear strength. In compounds where the loading or particle size reduces tensile strength and elongation of the unfilled compound, tear strength generally shows similar reduction. In comparing tear strength of PVC filled with treated and untreated calcium carbonate, there are conflicting effects. Untreated grades may be expected to form stronger points of polar attraction, strengthening the composition with regard to tear, but treated grades lead to better dispersion. Calcium carbonate of 1 μm mean particle size is thought to be optimum.

Calcium carbonate provides a modest increase in volume resistivity in PVC, but very much less than calcined clay. One can expect 10–20 phr to approximately double volume resistivity at constant plasticizer level. Usually, however, loadings of calcium carbonate are accompanied by increases in plasticizer level. For a typical ester plasticizer, the decrease in volume resistivity from increased plasticizer offsets, or more than offsets, the decrease from adding filler. This can be avoided by using combinations of calcium carbonate with the minimum needed level of ester plasticizer, plus a secondary plasticizer having good electrical properties, such as chlorinated paraffin (Paroil®, Dover Chemical) or polymerized aromatic oil (Kenflex® A, Kenrich Petrochemical). These approaches are typically used in jacket compounds having insulation resistance specifications. Insulation compounds are better served with calcined clay, or blends of the latter with treated calcium carbonate.

It is usually easier to stabilize a filled than a clear compound. Calcium carbonate can absorb a certain amount of hydrogen chloride and can serve as a secondary stabilizer, if levels of transition metals are very low. The presence of more than trace levels of, for example, iron will reverse this, again stressing the importance of using the correct grade. In addition, it is likely that low levels of inert filler can boost stability by increasing the effective distance between polymer chains, promoting stabilizer mobility. Further, there is some thought that filler can retard the loss of plasticizer through volatility, particularly at high plasticizer levels. The comparison is, however, not unequivocal. Stabilizer systems designed for clear compounds can differ considerably in level of metals and in type of organophosphite employed. Thus, the generalization that fine-particle calcium carbonate leads to longer color hold and failure time with a given stabilizer is not of any practical significance. Stabilizer systems can be designed to yield useful performance with almost any grade of calcium carbonate.

The addition of filler typically increases brittle point temperature and low-temperature stiffness. At high levels of plasticizer and with low-temperature plasticizers such as DOA or DOS, this effect is minimal with the usual loadings (10–50 phr) of calcium carbonate. Thus, in compounds formulated for low-temperature service, modest levels of calcium carbonate have little or no effect on performance.

Modest levels of calcium carbonate have essentially no effect on limiting oxygen index (LOI), as is the case generally with inert fillers. If filler addition prompts addition of increased levels of plasticizer, LOI may increase or decrease, depending on whether the plasticizer is combustible (esters or hydrocarbon secondary plasticizers) or flame-retardant (phosphate esters, halogenated esters, or chlorinated paraffin). On the other hand, calcium carbonate, particularly in fine-particle grades, reduces smoke generation in both flaming and nonflaming modes. This is interesting and apparently has not been investigated mechanistically. Usually, smoke suppressants function by promoting the reaction of elemental carbon (i.e., the smoke particles) to carbon monoxide. Often, this employs the “water gas” reaction:

$$C + H_2O \rightarrow CO + H_2$$

This reaction is catalyzed by metals that form metal carbonyls, such as molybdenum or traces of iron found in ATH. During combustion, it is possible that carbon dioxide liberated by calcium carbonate might function similarly:

$$C + CO_2 \rightarrow 2CO$$

Other reactions might be postulated; the subject is worth further investigation. Calcium carbonate, in fine particle grades, notably reduces hydrogen chloride emission during combustion. At least one grade, Ultracarb®, is sold for this purpose. It is often used in combination with flame-retardant fillers such as ATH and magnesium hydroxide.

Calcium carbonate reduces water and soapy water extraction of ester plasticizers used in flexible PVC, the effect increasing with higher loadings of filler (as plasticizer mobility is decreased). This tends to be the case with all fillers. Calcium carbonate filler will not prevent the loss of water-soluble compounding ingredients such as glycerol or pentaerythritol. Loss of such water-soluble polyols can be inhibited by inclusion of reactive species, such as benzoic acid, where the reaction product is insoluble. Calcium carbonate also increases resistance to extraction by mineral oil, up to a point (typically 30–50 phr filler) above which the extent of extraction increases. Studies with fluids of intermediate polarity and with a range of different fillers have yet to be reported, despite obvious practical interest. Calcium carbonate-filled compounds have good resistance to aqueous alkaline environments, but their use is dubious in the presence of aqueous acids. If exposure to acid is required, wollastonite would be a better choice.

At the levels at which calcium carbonate is used in rigid PVC for outdoor service, grades in the range of 1–3 μm particle size appear to have very little effect on weather resistance. Such studies of course feature compositions adequately protected by titanium dioxide or other UV light absorbers. Since the presence of low levels of calcium carbonate tends to improve titanium dioxide dispersion, its use is at least indirectly beneficial. Grades used in such applications should be very low in iron and other transition metals. With suitable protection from UV light, all of the fillers described in the foregoing could be used in exterior applications if warranted on other grounds. There is indication that use of fine (0.5 μm) and ultrafine (0.7 μm) precipitated calcium carbonate can enable reduction of titanium dioxide level with retention of long-term color hold, particularly if the starting level of the latter is quite high (e.g., 10 phr). Whether this remains the case with commercially used titanium dioxide levels deserves investigation.

The impact resistance of a polymeric composition depends upon its internal strength, itself deriving from chain-to-chain polar attraction and from shear modulus, a reflection of molecular weight. Very high-molecular-weight polymers, such as natural rubber, tend to deflect propagating cracks in circular rather than straight line patterns. This is not the case with PVC and polymers of similar (or lower) molecular weight. In such cases, there are two methods of improving impact resistance. With rigid PVC, it is important to retain structural load-bearing capability. Propagating cracks from impact are defeated by use of small insoluble particles that intercept the growing crack and transform it into a number of radiating microcracks or crazes, absorbing the energy delivered by impact. For a particle to function in this manner, in addition to being insoluble, it must be of a correct size, typically about 1 μm, be well distributed in sufficient quantity, and have strong adhesion to the polymer matrix. Without strong adhesion, the propagating crack simply bypasses the particle inclusion. Impact modifiers, particularly core–shell types, meet these requirements. It is widely thought that if an impact modifier has elastomeric character, then that additional impact energy is absorbed. (This is a matter of a certain degree of controversy. Some investigators believe that the effect is very minor.)

A second method of improving impact resistance is to convert the mechanism from brittle to ductile failure; that is, to provide means for the composition as a whole to absorb the impact energy without crack propagation. This approach lowers stiffness and load-bearing capacity and is directed generally to flexible and semirigid compositions. For example, an increase in lubricant level will usually lead to greater impact resistance at the expense of reduced structural strength. This is rarely useful in rigid PVC formulating.

Fine-particle and ultrafine precipitated calcium carbonate can act as impact modifiers for rigid PVC at levels of 10–20 phr, particularly with medium- and high-molecular-weight resins (very little improvement is found with low-molecular-weight PVC). Similar results are found with submicron silica (Sidistar®, Elkem). The best practical approach for the formulator is to evaluate combinations of organic impact modifiers and fine-particle fillers. An interesting approach would be to investigate submicron titanium dioxide (a UV light absorber but not a pigment) in this regard, particularly in dark-colored exterior rigid PVC.

A problem associated with impact strength determination is that standard methods in use (notched Izod, falling weight, and dart impact tests) often have poor correlation. It would be of interest to develop DMA procedures to simulate field service impact situations.

Whether surface treatment of the filler will improve impact resistance depends on the extent to which adhesion to the polymer matrix is improved. For example, treatment of submicron calcium carbonate with a titanate surface-active agent (KenReact® 238S, Kenrich) at a 1 percent level provides improved impact strength, presumably as a monolayer is formed on the filler surface. Use instead of 3 percent, forming a surface multilayer, an adhesive weak point, lowers impact strength as compared with no treatment.

6.2.4 Calcium Carbonate Selection

Rigid PVC PVC pipe for pressurized applications typically contains low loadings (5–10 phr) of 1 μm calcium carbonate, occasionally submicron grades. Drain, waste, and vent (DWV) pipes often use 30–50 phr of 3 μm filler, sometimes blends of various grades. Both products are almost invariably twin-screw extruded. Electrical conduit is similar; sometimes surface-treated grades are used, particularly, with single-screw extrusion (which has persisted in this industry in North America). Extruded profiles tend to use 5–20 phr of 1 μm filler; if foamed, generally less. High-impact grades of vinyl siding substrate contain 5–20 phr of 1 μm grades; capstock layers use lower levels. Extruded blinds are found with up to 50 phr of 3 μm calcium carbonate, sometimes less if reprocessed from siding or profile scrap. Injection-molded articles generally use 1 μm filler; extruded and calendered sheet, 1 and 3 μm grades.

Flexible PVC Wire insulation generally uses 5–25 phr of 3 μm grades, depending on the application; jackets and molded electrical connectors, as high as 50–60 phr.

Extruded weatherstrip and gaskets again use 3 μm filler; hose components typically 1 μm. Injection-molded footwear and electrical connectors use relatively high loadings of 3 μm calcium carbonate (≥25 phr). Blends of fine- and coarse-particle calcium carbonate are used in calendered sheet flooring (50–150 phr) and in floor tile (100–800 phr). Extruded cove base typically uses high loadings of coarse and fine blends in the substrate layer and 1–3 μm filler in the topcoat. Cove base substrate and flooring components are excellent areas for experimentation with blends of calcium carbonate with silicate fillers.

Roofing and pond liners typically use 20–50 phr of 3 μm filler; opaque shower curtains and vinyl upholstery more commonly use 1 μm grades at 10–25 phr. Calendered film and sheet used as decorative coverings for luggage and automotive components may use submicron grades where very fine detail is needed in postfinishing operations, or 1–3 μm grades in less demanding applications. Plastisol-coated carpet backings commonly use blends of fine- and coarse-particle calcium carbonate; automotive upholstery coatings, 3 μm filler.

6.3 SILICATES

Minerals of the silicate family have found use in PVC based on the anticipated property improvements that each type would provide. This group includes wollastonite, talc, kaolin, mica, feldspars, and nepheline syenite. Typically, this family is mined in areas where the ore is of commercially significant occurrence. All members of this group are found in North America. Processing methods to beneficiate the crude ores to desirable end products include air flotation, wet milling, froth flotation, and dry grinding. Because metallic contaminants can be associated with these ores, a common practice is to include electromagnetic separation to remove these materials (which often have commercial value).

Silicate minerals have a lattice structure, which is determined by the particular silicate's coordination chemistry. This combination of structure and chemistry can play a huge role in how the mineral will behave in polymer matrices. Surface chemical properties can determine compatibility with the polymer and with other additives or coupling agents. Particles in the silicate group can be described as having three basic shapes:

- Platy, as in talc, mica, and kaolin clay
- Nodular (i.e. lump-like), as in feldspars and nepheline syenite (an igneous mineral of structural similarity to feldspar)
- Acicular (needle-like), as in wollastonite

For the platy and acicular forms, aspect ratio is useful in describing the shape. For instance, the aspect ratio of a selected wollastonite grade could be 14 : 1, meaning that the length, on average, 14 times the diameter. For platy forms, the aspect ratio is the relationship of thickness of the plate compared to the diameter across the face of the plate.

Silica itself (the simplest "silicate") has found little use in PVC because of its abrasivity (Mohs hardness of 7) and its acidity (pH 6–6.5), having been superseded as an antiblocking agent by zeolite and various silicates. An exception is diatomaceous amorphous silica, which, in synthetic forms (Celite®) and as naturally occurring diatomaceous earth, is often used as the carrier in dry liquid dispersions. Diatomite is less abrasive than other forms of silica (Mohs hardness of 5–6) and is pH-neutral. It is an excellent solid carrier for polymeric plasticizers of viscosity high enough to make handling difficult.

Recently, a spherical form of silica has been introduced by Elkem under the trade name Sidistar®. This product has the right particle size distribution to serve as an impact modifier and may provide synergistic improvements with organic additives (Chapter 10). Blends with calcium carbonate and with high-aspect-ratio fillers should be of interest in rigid PVC.

Although widely used as a reinforcement in other plastics, glass fiber has found limited use in PVC. The main application is in plastisol- and latex-saturated glass fabric carpet backings. In this case, PVC is a protective coating for the fiber rather than a compound reinforced by it. It is, therefore, similar to PVC-coated polyester fabric commonly used as flexible backgrounds for signs and displays. Rigid PVC compounds with loadings of 10–30 percent glass fiber are available from PolyOne under the trade name Fiberloc®.

6.3.1 Talc

Talc, hydrous magnesium silicate, has the formula, $Mg_3Si_4O_{10}(OH)_2$ (this is a better description of its chemistry than the commonly found $3MgO \cdot SiO_2 \cdot H_2O$). Also known as soapstone, the mineral naturally occurs as essentially a white, or greenish-white mineral. Physically, talc is soft (Mohs hardness of 1) and nonabrasive, with a characteristic platy shape. With this shape and the relative inertness, talc can be effective in increasing stiffness and dimensional stability. In New York, another form of talc is mined and processed, a tremolitic (i.e., containing calcium silicate as well as magnesium) talc. This form has basically three different shapes: platy, blocky, and acicular. It has a higher Mohs hardness than the typical platy talc: 4 versus 1.

Most of the commercially known grades of talc are processed to have average particle diameters of 1–15 μm. Specific gravity ranges from 2.7 to 2.8 and the pH is alkaline (about 9). The latter suggests use in crosslinked PVC since free radical cure systems are sensitive to acid fillers. In general, the use of an alkaline filler tends to add to PVC heat stability. Talc fillers are supplied by Luzenac, Zemex, Specialty Minerals, and R.T. Vanderbilt.

Talc at present is not often used in PVC, either in rigid, flexible, or plastisol compositions. Current uses in PVC compounding include reducing plateout, controlling crease whitening in PVC-based credit card stock, and as a flow aid for PVC pellets, where it is used at 0.1–0.2 phr. Silane surface treatment of talc as been used in a number of applications in polyolefins, polyesters, and polyamides. Either an aminosilane or a mercaptosilane could be used to bond talc particles to PVC, the silane alkoxy groups condensing with —OH on the filler and S—H or N—H groups displacing labile chloride from PVC. Such treatment would increase flexural modulus, and is worth considering for structural applications. Talc surface treated with triethoxy caprylyl silane is available commercially (Kobo Products, U-1152). This type of silane is not PVC-reactive, but will increase hydrophobic character and is likely to aid processability.

Although talc is more expensive than the lowest-cost grades of calcium carbonate, the properties of low-equipment abrasion and functional reinforcement suggest that its use should be considered more broadly by the formulator.

6.3.2 Kaolin

Kaolin clay is hydrous aluminum silicate, with the formula $Al_4,Si_4O_{10}(OH)_8$. (Other types of clay, such as bentonite, are rarely used in PVC.) Characterized by a platy shape, kaolin is generally described as a white, soft, and plastic clay. In contrast to other platy silicates, kaolin clay platelets occur in nature as stacks or booklets. Kaolin can be processed simply by crushing, drying, and grinding (air flotation), water washing (wet processing), and further refined under high heat (calcination). The goals are to remove localized impurities, delaminate the physically bound platelets, and to stabilize the surface chemistry. Commercial forms of kaolin clay have average diameter ranging from 0.3 to 5 μm. Both air-floated and calcined versions can be surface-treated with various silanes. The treatment affords both improvements in mechanical strength properties, such as improved impact resistance, and also in processing, such as improved dispersion and ability to carry higher loadings.

Untreated kaolin clay, available in "soft" (more highly hydrous) and "hard" (less so) grades, although widely used in rubber compounding, finds little use in PVC. Calcined clay, on the other hand, is widely used in electrical applications. It is a better insulator than PVC itself (most plasticizers are worse). The extent to which addition of clay improves the volume resistivity of plasticized PVC is striking. It is likely that the plate-like nature of calcined clay interferes with electrical leakage paths through the composition. Addition of calcined clay to plasticized PVC provides some improvement in dielectric constant and power factor, but the major improvement is in insulation resistance (which depends upon volume resistivity). A typical wire insulation formulation might comprise:

PVC	100
DIDP	52
ESO	3
Tribasic lead sulfate	5
Stearic acid	0.3
Calcium carbonate	10
Calcined clay	10

The effects on volume resistivity (VR) of the addition of calcined clay are major. With 10 phr calcium carbonate and no clay, VR is 340×10^{11} ohm-cm at room temperature, dropping to 1.9×10^{11} ohm-cm at 70 °C. The addition of 10 phr calcined clay increases VR to over 2000×10^{11} ohm-cm at room temperature, and to 13.2×10^{11} ohm-cm at 70 °C. Physical properties and heat stability are essentially unchanged.

With proper choice of plasticizer and stabilizer, formulations using blends of clay with small amounts calcium carbonate can pass long-term wet electrical testing requiring stable (within limits) insulation resistance (IR) in 75 °C water. These tests are run on wire samples subjected to 600 V, the water tank being grounded. Typically, if insulation resistance levels off in 10–20 weeks, it will remain level or may actually rise as the test is carried to 6 months. Two factors are in play. Entrance of water into the compound, driven by attraction to water-soluble ingredients, drastically lowers IR. Compounding ingredients are chosen carefully to minimize such inclusions. In addition, many stabilizers, such as those based on basic lead compounds and, more recently, on hydrotalcite, will complex ionic impurities, lowering the drive to entrance of water. High compound modulus will also assist. If IR levels off, the 600 V potential tends to drive ionic materials out of the insulation into the water tank. Thus, a balance of ionic strength is established. It is important, for consistent results, never to change the water in the tank during long-term testing. When tests are run, instead, in 90 °C water (UL Type THWN-2), only calcined clay or silane-treated calcined clay should be used as filler.

It should be noted that long-term wet electrical tests are run on PVC wire coverings almost exclusively in North America. In other parts of the world, such properties are not considered significant, and, as a result, calcium carbonate is used as filler rather than clay. The rationale is that PVC wire coverings are not used in water-submersible constructions and that, therefore, long-term behavior in water is irrelevant. Indeed, PVC is a poor choice for submersible cable as compared with XLPE or EPDM. On the other hand, conformation to UL and CSA standards requiring long-term electrical stability in water has led to products such as building wire of exceptional quality and durability (if not profitability).

Clay has a specific gravity (most grades) of 2.6 and is easy to disperse in all types of mixing equipment. Calcined grades have Mohs hardness of 4–6 and are a factor in abrasive wear of equipment. In addition, having pH values of 5–6, no additional heat stability is imparted to PVC. Besides its use in wire insulation, calcined clay has been used in plastisols in blends with calcium carbonate to modify viscosity. Its higher cost compared with calcium carbonate is a barrier to other than special purpose use. Calcined clay is supplied by Burgess Pigments, Engelhard, Huber, Imerys, and R.T. Vanderbilt.

6.3.3 Mica

The term “mica” includes a whole family of aluminum silicates. Commercial grades differ in the ratio of aluminum to magnesium found (with potassium) in the cationic portion of the mineral crystal. The two prevalent commercial types are

$KAl_2(AlSi_3)O_{10}(OH,F)_2$, muscovite, and $KMg_3(AlSi_3)O_{10}(OH,F)_2$, phlogopite. Both are somewhat harder than talc (Mohs hardness of 2–3) but, since they are platy in nature, are softer and less abrasive than calcium carbonate. Mica fillers have a specific gravity of about 2.8 and are slightly alkaline (pH about 8).

Micas are typically depicted as sheet silicates and, as with other fillers, are processed using wet and dry grinding techniques. Micas can also be further micronized to below 1 μm particle size. For the plastics industry, generally commercial grades range from 2 to 40 μm. Limiting factors in use are color and wide variation in decomposition temperature and water content. Mica is often surface-treated with either silanes or titanates. A grade treated with triethoxy caprylyl silane is available commercially (Kobo Products, GMS-1152). This type of treated product should be useful in calendered film for imparting a low surface energy. It is likely also to be helpful in incorporation. Typically, mica is not easy to disperse, and should be mixed with high-shear equipment. Mica fillers are supplied by Engelhard and Specialty Minerals.

In PVC, mica improves flexural strength and stiffness. Although now used most often as an antiblocking agent (1–3 phr), the combination of structural reinforcement and dimensional stability of mica-filled PVC warrants further investigation by formulators. In rigid compounds, replacement of calcium carbonate with mica, or addition with calcium carbonate, notably increases flexural strength and modulus, while significantly lowering the coefficient of thermal expansion. The problem is, of course, how to turn such advantages into salable commercial products.

6.3.4 Feldspar and Nepheline Syenite

Feldspar and nepheline syenite (Minex®) are aluminosilicates differing in varying levels of potassium (K), sodium (Na), and calcium (Ca). Further, nepheline syenite is often described as silica-deficient feldspar. It is apparently naturally produced in the evolutionary development of bauxite. Whereas feldspar contains 67 percent silica and 18–19 percent alumina, nepheline syenite contains 60–62 percent silica and 22–23 percent alumina. So-called "soda" feldspar further contains about 2 percent calcium, 4 percent potassium and 7 percent sodium, as their oxides. "Potash" feldspar is found with less than 0.5 percent calcium, about 12 percent potassium, and 2 percent sodium, as their oxides. In an intermediate position is nepheline syenite with low calcium, 10 percent sodium, and 5 percent potassium. At comparable particle size, this group can functionally be considered a single filler. Various grades are supplied by Unimin.

The particle morphology differs from other aluminosilicates in that the aspect ratio is close to one. The shape is blocky or irregular. For commercial grades of feldspar, the average diameter range is 3–16 μm, and for nepheline syenite, the range is 2–16 μm. Both are characterized by comparatively low oil absorption. Conventional dry processing techniques are used, in combination with electromagnetic separation, to create the particle size ranges. Feldspar is of low cost, and has a specific gravity of 2.6 and a pH of 7–8. Minex® (Unimin Specialty Minerals) is also of low cost, with a specific gravity of 2.6, but a pH of 10–10.5.

In plastics applications generally, feldspar improves stain, abrasion and chemical resistance. Feldspar and nepheline syenite (Minex®) have been used in high-traffic vinyl flooring and PVC cove base molding. Micronized Minex® has gained interest as a low-cost filler, exhibiting low resin demand, thus enabling high loadings. Other reinforcement properties are excellent dimensional stability, impact strength, and high heat deflection temperature. A very useful property is that, with a refractive index of 1.53, both fillers closely match plasticized resin, resulting in translucent or more or less clear compounds, depending on loading and particle size. Loadings of 5–10 percent of the finer grades produce translucency appropriate, for example, for shower curtains. The incorporation, where possible, of a filler of alkaline pH tends to improve PVC heat stability. More complete data can be found in the product brochures from Unimin Specialty Minerals.

Minex® has a Mohs hardness of 5.5–6, feldspar, 6–6.5. The hardness at which steel equipment is scratched is about 5.5, depending upon the grade. With ordinary mixing equipment, both fillers should be added in dry blending operations after incorporation of plasticizer, so as to minimize shear stress, and the mix completed as rapidly as possible. Similar procedures should be followed in Banbury® and in plastisol mixing. Incorporation is typically very rapid. Use of fine particle grades will minimize abrasive loss of metal. Extrusion and pelletizing should emphasize streamline flow so as to avoid metal contamination and discoloration. If use of large quantities of fillers with high hardness is contemplated, consideration should be given to special purpose plating of equipment surfaces.

6.3.5 Wollastonite

Chemically calcium metasilicate ($CaSiO_3$), wollastonite has the theoretical composition of 48.3 percent CaO and 51.7 percent SiO_2. It is unique among the naturally occurring minerals in that it is the only one that is white, nonmetallic, and acicular in particle shape. Wollastonite is processed primarily by dry grinding and electromagnetic separation. Where calcite is prevalent in the ore, froth flotation can be used to produce a wollastonite concentrate. Because of its special needle- or shard-like shape, wollastonite is marketed in both a low-aspect-ratio ($<5:1$) powder form and high-aspect-ratio (about 12–15 : 1) versions. It has a specific gravity of 2.9 and is alkaline (pH 9.9), with a Mohs hardness of 4.5, slightly less than will scratch steel. In compositions pigmented with titanium dioxide, the alkaline nature of wollastonite adds to color hold in both heat stability and weatherability tests.

Wollastonite is very amenable to organosilane treatments, and is often treated with reactive groups such as amino, epoxy, vinyl and methacrylate. Amino- and mercaptosilanes will bond the filler to PVC; the others can assist in various crosslinking mechanisms. In recent years, silanes with nonreactive groups, such as dialkyl ligands, have also been utilized. Although not producing resin–filler bonds, these silanes improve ease of dispersion and reduce abrasivity. It is likely that titanate or zirconate treatment will provide similar results.

Wollastonite originally replaced asbestos in formulations for vinyl asbestos flooring. However, as that industry has changed to other compositions, the cost of wollastonite has limited its growth. Recently, wollastonite has been considered for use in providing improved modulus and flexural strength in rigid and flexible PVC. It is possible that wollastonite can be a partial replacement for glass fiber with cost savings, without sacrificing reinforcement. The area of reinforcement of PVC with high-aspect-ratio fillers is one deserving of more attention by the formulator. This area was virtually eliminated by reaction to asbestos toxicity. It should not extend to biologically inert high-aspect-ratio fillers such as wollastonite, which is by its nature a good candidate to explore in blends with calcium carbonate in floor tile.

In one study, in a low voltage insulation, wollastonite showed interesting properties compared to calcium carbonate. The base compound comprised:

PVC (Geon 30FG)	100
DIDP-E	50
ESO	5
Ca/Zn stabilizer	2
165 wax	0.5
Filler	40

Comparing 3 μm wollastonite (Vansil® W-50, Vanderbilt) with 3 μm calcium carbonate (Atomite®, ECC), although modulus at 100 percent and 200 percent was similar, modulus reflecting service conditions, 25–50 percent, was notably higher. This is typically a plus, reflecting increased cut through and chemical and abrasion resistance. The same conclusion applied to a comparison of 5–6 μm fillers (Vansil® W-40 wollastonite versus Vicron® 25–11 calcium carbonate (Specialty Minerals)). In both cases, wollastonite yielded longer failure time than calcium carbonate in 190 °C static heat aging. These conclusions carry over to 50/50 blends of calcium carbonate or wollastonite with calcined clay in the above formulation. What is particularly interesting to the formulator is that the wollastonite/calcined-clay blend could be silane-treated for improvement in electrical properties, imparting a hydrophobic surface to the entire blend. Wollastonite is supplied by Nyco and R.T. Vanderbilt.

6.3.6 Compounding with Silicates

When using silicate fillers, consideration is required not only of the chemistry, but also of particle size and shape. Mechanical strength and electrical properties are important formulating parameters, as these cover basically all PVC end uses. Not all fillers are suitable for PVC, and in some instances, the cost of these fillers versus conventional loadings of calcium carbonate will preclude serious consideration. With increasing performance demands, however, especially in the building products area, nontraditional functional fillers may find acceptance. Where surface treatment without filler coupling is indicated (to improve incorporation and dispersion), aluminum distearate is a good choice. In general, the best results with stearate coating are found when the stearate cation matches that of the filler or is closely compatible.

6.4 SULFATE FILLERS

Barium sulfate (barite, barytes) has been used sparingly in PVC for many years. It is of neutral pH and low abrasivity (Mohs hardness of 3–3.5) and is readily dispersed in a variety of polymers. Its main characteristic is its high specific gravity, 4.35. Thus despite its low cost, pound–volume costs are high. It is used where added weight is desired without a high pigmentation value (such as would be found with titanium dioxide). Examples are in vinyl curtains to improve drape and in slip-resistant floor mats. Where best color is needed, the more expensive precipitated version, blanc fixe, should be used. Barium sulfate fillers provide dimensional stability and good chemical resistance. The high specific gravity is useful in blankets for X-ray protection. On the other hand, this would make it a poor choice for crosslinked PVC products. If surface treatment is indicated to improve dispersion, barium stearate is a good choice.

Anhydrous calcium sulfate also finds occasional use in PVC. It has higher brightness than calcium carbonate and is softer (Mohs hardness of 2–3). It is, in addition, a basic filler (pH 10) that adds to stability. There has been use in plastisols, particularly for foamed articles requiring high brightness, such as in flooring components, and in extrusions, both rigid and flexible. Dispersion is rapid, but, as also with storage, moisture must be excluded to prevent formation of hydrated calcium sulfate, a crystalline, difficult-to-disperse product. It is this characteristic that has limited its use in PVC. Surface treatment with calcium stearate provides an improvement and aids in dispersion.

6.5 CARBON BLACK

The use of carbon black as a pigment in PVC is discussed in Chapter 5, and its use as a UV light absorber in Chapter 4. Another important use is to provide semiconducting properties. There are two areas that differ significantly: conduction so as to drain surface charge to ground or to air, and the conduction needed in cable semiconducting layers. The first area is discussed under antistatic agents in Chapter 12. Typically, a surface resistivity of about 10^{10} ohm is needed. Cable semiconductors and layers to block RF transmission, on the other hand, require a volume resistivity of $10–10^3$ ohm-cm. The region can be reached with PVC compositions containing 20–30 percent of extra conductive furnace (ECF) black (e.g., Vulcan® XC-72, Cabot) or 10–15 percent of ultra conductive black, such as Ketjenblak® (Akzo Nobel). The level depends greatly on the type and level of plasticizer, phosphates tending to yield the lowest values.

Conduction in carbon black-filled composites depends on close contact between particle aggregates. It is thought that leakage current through one aggregate induces a corresponding flow of charge in adjacent ones. It is important, therefore, not to break down aggregates into primary particles by overmixing. Thus, in mixing, the goal here is good distribution, not dispersion. Conductive black should be added after plasticizer uptake is complete and the batch completed rapidly. If incorporation and uniform distribution proves a problem, often best results are obtained with blends of a major fraction of conductive black with a minor amount of a black that incorporates easily, such as SRF of GPF.

Filled PVC/VA phonograph records use low levels (0.5–2 phr) for a combination of pigmentation and static dissipation; the filler is generally calcium carbonate.

6.6 MICROSPHERES

The use of hollow glass or ceramic microspheres enables manufacture of articles of low specific gravity without the use of blowing agents and the sophisticated technology needed to produce consistent expanded products. Balanced against this is the relatively material cost of microspheres and the need for low-intensity mixing and processing to avoid breakage, This has tended to limit applications to special products, particularly those based on plastisols. Current applications include carpet backings, automotive undercoats, and floating fishing lines. Products are supplied by Akzo Nobel (Expancel®), Emerson & Cuming (Eccospheres®), Microsphere (Cenospheres®), PQ (Sphericell®), Sekisui (Advancell®), and Sovereign (Micropearl®). Specific gravity is generally between 0.2 and 0.5. Although silicates, the spherical shape mitigates against equipment abrasion.

Solid glass microspheres are also available (Spheriglass®, PQ Corp.) and are useful in improving dimensional stability of injection-molded rigid PVC. Solid microspheres are able to withstand high-intensity processing. An interesting development has been that of expandable microspheres, which can survive considerable shear in mixing and processing and then expand, typically at about 200 °C. Products are available from Akzo Nobel (unexpanded Expancel®) and Sovereign (Dualite®). The innovative PVC formulator may find use for such products.

6.7 COUPLING AGENTS

Coupling agents are used to modify polymers to provide sites for reaction (see Section 3.4) or to promote adhesion (see Section 12.7). They are more frequently used to modify filler surfaces to improve incorporation and distribution, to improve electrical properties, and, in some cases, to cause bonding of the filler to the polymer, improving modulus and resistance to deformation. A coupling agent has the general formula

$$(\mathrm{R'{-}O})_n\mathrm{{-}M{-}R{-}X}$$

In the above, M is usually silicon, titanium, or zirconium; thus, often $n = 3$. X is a functional group that can react with the polymer: a mercapto or amine group in the case of PVC. R is the organic group that links the reactive group to the coupling agent. It should have thermal and chemical stability at least equal to that of the polymer. In reactions in which filler is bonded to the polymer, increasing the number of carbon atoms in the R group typically provides increased flexibility at the expense of modulus. If M contains two —R—X groups, then n is reduced from 3 to 2. R′—O— should be a good leaving group from M, readily converted to HO— by water on the filler surface. The HO—M product readily condenses with —OH groups on the filler surface, bonding the coupling agent to the filler. The intermediate HO—M product can also self-condense, forming a gel structure or intractable lumps. It is therefore important to add coupling agents to an excess of filler to prevent self-condensation. At the levels used (typically 1 percent of the filler), correct addition rarely produces problems. Use of excess coupling agent, often with titanates and zirconates, may cause self-condensation onto the treated filler surface, commonly defeating the goal in treatment. With titanates and zirconates, suppliers' instructions should be followed closely. It should be noted that when used as adhesion promoters or to provide sites for reaction, the coupling agent should be added to the polymer for reaction therewith, and fillers with surface —OH groups avoided.

Coupling agents are moisture-sensitive. Partial hydrolysis may cause loss of activity and lump formation. If such problems occur, there are two general solutions. One is to purchase pretreated filler; many grades are available. Alternatively, coupling agents are available encapsulated in paraffin wax as a barrier to atmospheric moisture. Both solutions also avoid the flammability hazard associated with pure coupling agents, which are typically volatile and excellent fuel sources. Coupling agents to bond fillers to PVC are supplied by GE (A-189, A-1891 mercaptosilanes; A-1100, A-1110 aminosilanes), Dow Corning (Z-6062 mercaptosilane; Z-6020, Z-6026 aminosilanes), Degussa (CM8500 mercaptosilane; CA0750 aminosilane), Cavedon Chemical (MOD S mercaptozirconate; MOD A aminozirconate), and SCM (Prosil 196 mercaptosilane; Prosil 321 aminosilane). In addition, additives for filler surface treatment are supplied by Kenrich (LICA 38, KR TPP titanates; KZ TPP zirconate).

Certain coupling agents are helpful in blends of PVC with reactive polymers such as urethanes. These are the polyaminosilanes used also as adhesion promoters: A-1120 and A-1130 (GE); CT2910 (Degussa); and Z-6050 (Dow Corning). Another such group is that of ureidosilanes: A-1160 (GE), CS1590 (Degussa), and Z-6032 (Dow Corning). These are also useful in PVC/ABS blends.

Aminosilane coupling agents such as A-1100 are also used with wood fiber vinyl composites. This subject is discussed in Chapter 17.

CHAPTER 7

Monomeric Plasticizers

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7.1 INTRODUCTION

There are two primary technologies to create a flexible PVC product: either one can add a "flexibilizer" or a plasticizer to the PVC polymer or one can chemically modify the PVC molecule. For the formulator, the preferred method is to add an external plasticizer. External plasticization describes the addition of a plasticizer to the rigid polymer, where the level of flexibility can be adjusted by both the type and level of the plasticizer. The choice of plasticizer can be complex because of the wide variety of products available and the different effects that can be achieved. To simplify the plasticizer choice selection, several plasticizer classification schemes have been developed.

The two primary plasticizer classifications are monomeric and polymeric. The term "monomeric" is used to describe plasticizers that are characterized by a single or simple molecular structure. Generally these plasticizers are esters, in a molecular weight range of 300–600, having low vapor pressure and good heat stability, and are for the most part, chemically inert. In contrast, polymeric plasticizers are those products that are formed by repeating molecular units. Polymeric plasticizers have a broad range of molecular species, with molecular weight distributions varying from one product to another. The molecular weight of a polymeric plasticizer can range from 1000 to over 10,000, with somewhere around 3000 representing the typical product molecular weight. Polymerics offer lower volatility and greater permanence as compared with monomeric plasticizers, but the higher viscosities, the associated debits in processability, and the higher product costs limit their utility to those applications where the value of greater permanence can be realized in the price of the final product. The focus of this chapter is the use of monomeric plasticizers in achieving a flexible PVC product.

In 1951, The Council of the International Union of Pure and Applied Chemistry (IUPAC) adopted the following definition of a plasticizer: *a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility.* In addition, it is noted that a plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product, but it does not alter the chemical nature of the macromolecule.

This plasticizer definition is not specific to any chemical or material. It is solely a description of certain performance criteria. Unfortunately, these and other performance criteria cannot be easily predicted from the chemical or physical properties of the plasticizer, per se. Thus, it is necessary to define plasticizers by both the performance and chemical classifications.[1]

For the most part, plasticizers are added to PVC to make a product flexible. Some plasticizers are more efficient at this than others. In the course of formulating a product, it can be found that while some plasticizers will yield additional benefits such as improved performance at low or high temperatures, other plasticizers can contribute benefits such as reduced flammability. Yet other plasticizers may be simply chosen because they are inexpensive or have greater permanence or more favorable toxicity profiles. In the development of a flexible PVC formulation, the choice of monomeric plasticizer will have a significant impact on the performance of the flexible plastic and the overall cost.

7.2 MECHANISM OF PLASTICIZATION

One primary requirement for plasticization is that a plasticizer must be thoroughly mixed and incorporated into the PVC polymer matrix. This is accomplished by heating with mixing, until the plasticizer is incorporated into the resin. The plasticized material is then molded or shaped into the useful product and cooled. Different plasticizers will exhibit different characteristics in both the ease with which they form the plasticized material and in the resulting physical properties of the flexible product.

Since the concept of plasticization of PVC was first reported,[2] there have been numerous theories proposed to describe the plasticization effects. It is generally regarded that plasticization of PVC is a complex process, not capable of being described by a single theory, but only through a combination of theories. A significant review of the theoretical treatment of plasticization has been described by Sears and Darby[3] in their definitive text, *The Technology of Plasticizers*. In this treatment, the authors describe plasticization by three primary theories, with some modifications included in the discussions. A summary of these theories and others follow.

According to the *lubricating theory* of plasticization, as the system is heated, the plasticizer molecules diffuse into the polymer and weaken the polymer–polymer interactions (van der Waals forces). An analogy is offered whereby the plasticizer acts much like oil lubricating two pieces of moving parts. With this theory, the plasticizer molecules act as shields to reduce polymer–polymer interactive forces and prevent the formation of a rigid network. This lowers the glass transition temperature T_g of the PVC molecules and allows the polymer chains to move rapidly, resulting in increased flexibility, softness, and elongation. Although this effect may be easy to visualize, there are several problems with this concept, and the lubricity theory is rarely used by itself to describe plasticization of PVC.

The *gel theory* starts with the assumption that the rigidity of a polymer arises from a three-dimensional network of weak secondary bonding forces occurring along the polymer chains. The plasticizer acts upon this rigid or gel structure by disrupting the polymer–polymer attractions, inserting itself between these chains, and consequently reducing the rigidity of the gel structure. Some of the plasticizer molecules will solvate the resin at the point of attraction, while other plasticizer molecules cause the remaining gel structure to swell or to expand. As the rigidity is decreased through reduction of the gel structure, the polymer becomes more flexible.

Although some of these effects most likely occur in plasticization of PVC, again, this theory alone is not sufficient to describe the observed flexibility.

Free volume is a measure of the internal space available within a polymer. As free volume is increased, more space or free volume is provided for molecular or polymer chain movement. A polymer in the glassy state has its molecules packed closely but is not perfectly packed. Thus, the free volume is low and the molecules cannot move past each other very fast. When the polymer is heated to above T_g, the thermal energy and molecular vibrations create additional free volume, which allows the polymer molecules to move past each other rapidly. This has the effect of making the polymer system more flexible and rubbery. Free volume can also be increased through modifying the polymer backbone, such as by adding more side chains or end groups or by the addition of smaller molecules such as plasticizers to the polymer matrix. This lowers T_g by separating the PVC molecules, adding additional free volume and thus making the PVC soft and rubbery.

Other explanations are built upon these three theories. The *mechanistic theory* of plasticization considers the interactions of the plasticizer with the PVC resin macromolecules. It assumes that the plasticizer molecules are not permanently bound to the PVC resin molecules but are free to self-associate and to associate with the polymer molecules. As these interactions are weak, there is a dynamic exchange process whereby, as one plasticizer molecule becomes attached at a site or center, it is readily dislodged and replaced by another. Different plasticizers yield different plasticization effects because of the differences in the strengths of the plasticizer–polymer and plasticizer–plasticizer interactions. At low plasticizer levels, the plasticizer–PVC interactions are the dominant interactions, while at high plasticizer concentrations, plasticizer–plasticizer interactions often become more significant.

Infrared and nuclear magnetic resonance (NMR) studies of plasticized PVC products show that the plasticizer molecules interact with PVC only in the amorphous region of the PVC molecular structure, leaving the crystalline regions of the polymer free of plasticizer. In general, they have found little evidence for "pools" of plasticizers.[4] In a more recent study using NMR techniques combined with molecular modeling,[5] Howick concludes that it is not the polarity of the plasticizer that determines the overall effectiveness of a plasticizer. He found that as the polar center of the plasticizer interacts with polar centers of the PVC molecule, this interaction can impact the ability of the alkyl chains of the plasticizer to create free volume. It is this effect that determines the efficiency of the plasticizer; those interactions yielding a greater free volume contribution arising from the alkyl side chains are the more efficient plasticizers.

When the PVC polymer and the plasticizers are heated, the plasticizer begins to solvate portions of the PVC polymer. Initially, these interactions take place only in the amorphous region of the polymer; but with continued heating and mixing, the crystalline regions melt, and the PVC polymer in those regions begins to interact with the plasticizers. Upon cooling, a small amount of crystalline regions begins to reform; these regions are again void of plasticizer. In the amorphous region, though, the PVC polymer remains weakly associated with the plasticizers. Here, the plasticizer adds free volume, provides lubrications to the PVC chains, and helps in reforming an expanded, flexible polymer structure.

7.3 PLASTICIZER CLASSIFICATION

The selection of a plasticizer type is primarily determined by the performance requirements of the finished product or by special needs that may be required during processing, with the overall basic requirement to meet the needed cost targets. Of the approximate 100 commercially available plasticizers, some form of classification system is needed to help in this selection. Unfortunately, a single classification system is not sufficient in to predict the performance/cost benefits that a plasticizer can bring to the final product. Thus it is necessary to classify plasticizers by both their performance and chemical classifications.

The generally accepted categories for monomeric plasticizers based on their performance features are:

- General purpose (GP)
- Strong-solvating
- Low-temperature
- Low-volatility
- Other

Monomeric plasticizers may also be classified into six chemical families based on their chemical structures. These classes are as follows:[6]

- Phthalates
- Aliphatic dicarboxylic acid esters
- Phosphates
- Hydrocarbon extenders
- Epoxies
- Others

Plasticizers may also be further subdivided into primary and secondary types. Primary plasticizers are those used as the sole plasticizer or as the major component of the plasticizer system. Secondary plasticizers are typically blended with primary plasticizers to improve certain performance properties such as reduced flammability and improved processing, or simply to lower cost. Actually, there are some overlaps in these definitions, since some secondary plasticizers, can function as primary plasticizers when used at relatively low levels. An example is di-2-ethylhexyl adipate (DOA). DOA is often used as the sole or primary plasticizer in PVC meat wrap, typically at 30 parts per 100 of resin (phr). But it also functions as a secondary plasticizer when added at the 10 percent level to a general purpose plasticizer, for example to improve the low-temperature flexibility or flex rating of a PVC shoe sole. Other examples would include the use of a primary plasticizer, such the higher-molecular-weight phthalate diisodecyl phthalate (DIDP) for use as a minor component in blends with polymeric plasticizers to help improve processability or to lower costs.

7.4 PLASTICIZER PERFORMANCE COMPARISONS

To compare the performance of different plasticizers, it is important to have a point of reference. As the level of plasticizer is usually adjusted to give some measure of flexibility, the common practice is to compare plasticizers at the same level or degree of flexibility. This level is usually set using the plasticizer concentration required to give some measure of equal hardness or equal tensile modulus measured at 100 percent elongation. For example, Fig. 7.1 shows a comparison of the effectiveness of two general purpose plasticizers, diisononyl phthalate (DINP) and di-2-ethylhexyl phthalate (DOP or DEHP), in reducing Durometer A hardness as a function of plasticizer concentration measured in phr (i.e., the weight in pounds or kilograms of plasticizer used per 100 pounds or kilograms of PVC resin).

A quantitative measure of relative plasticizing efficiency is developed by determining the plasticizer concentration (in phr) required to meet a specific hardness versus some reference standard. For most applications, the reference standard chosen for PVC plasticizers is DOP. From the ratio of the DINP phr that is required to achieve a defined hardness to the DOP phr required for the same hardness, one develops a quantitative *substitution factor* (SF) for DINP versus DOP in providing equal hardness properties to the flexible PVC at room conditions. For example, to achieve at Durometer A = 80, 56.2 phr of DINP is required versus 52.9 phr DOP. Thus, the SF calculated for DINP is SF = 56.2 phr DINP/52.9 phr DOP, or 1.06. This means that for a given hardness, 6 percent additional DINP is required to give the same hardness as that obtained with DOP. While this example targets 80 Durometer A hardness, one may use this calculation at any specified hardness, or other property, required for the given end product of flexible PVC.

In this chapter, relative plasticizer performance properties are compared at 50 phr in unfilled PVC and at constant Durometer A hardness of 70.[7] The molecular weight and the substitution factors for the commonly used plasticizers are presented in

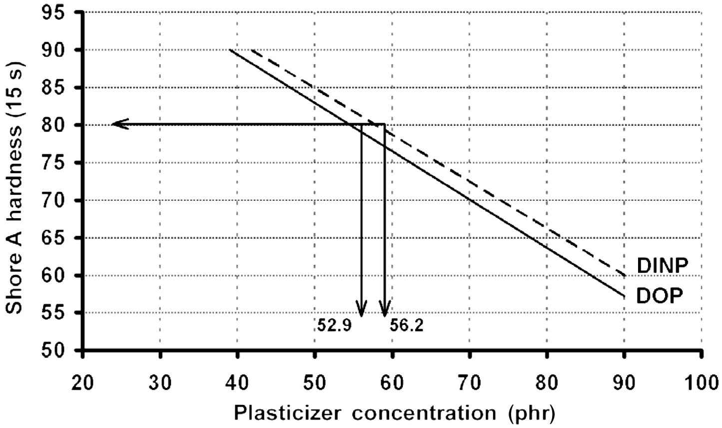

Figure 7.1 Shore a hardness versus plasticizer concentration.

TABLE 7.1 Plasticizer Acronyms, Chemical Structures, and Substitution Factors (SF)

Acronym	Chemical Structure	Molecular Weight	SF[a]
	Phthalates		
BBP	Butyl, benzyl	312	0.94
BOP	Butyl, 2-ethylhexyl	*ca.* 340	0.94
DnHP	n-Hexyl	334	0.96
DIHP	Isoheptyl	362	0.97
DOP (DEHP)	2-Ethylhexyl	390	1.00
DIOP	Isooctyl	390	1.01
DINP	Isononyl	418	1.06
DIDP	Isodecyl	446	1.10
DPHP	2-Propyl heptyl	446	1.10
DIUP	Isoundecyl	474	1.16
UDP	Iso C_{11}, C_{12}, C_{13}	*ca.* 502	1.21
DTDP	Isotridecyl	530	1.27
	Linear Phthalates		
DBP	n-Butyl	278	0.86
79P	Linear C_7, C_9	*ca.* 390	1.00
NHDP (610P)	n-C_6, C_8, C_{10}	*ca.* 418	0.99
L9P	Linear nonyl	418	0.99
7911P	Linear C_7, C_9, C_{11}	*ca.* 418	1.00
911P	Linear C_9, C_{11}	*ca.* 446	1.05
DUP (L11P)	Linear C_{11}	474	1.14
	Trimellitates		
NODTM	n-Octyl, decyl	*ca.* 592	1.12
TOTM	2-Ethylhexyl	546	1.17
TIOTM	Isooctyl	546	1.19
TINTM	Isononyl	588	1.27
	Adipates		
DOA	2-Ethylhexyl	370	0.93
DIOA	Isooctyl	370	0.94
DINA	Isononyl	398	0.98
79A	Linear C_7, C_9	*ca.* 370	0.91
	Phosphates		
DDP	Isodecyl, diphenyl	390	0.96
TOF	Tri(2-ethylhexyl)	435	1.00
TCP	Tricresyl	368	1.31

(*Continued*)

TABLE 7.1 *Continued*

Acronym	Chemical Structure	Molecular Weight	SF[a]
	Epoxides		
OET	2-Ethylhexyl epoxy tallate	*ca.* 410	0.96
ESO	Epoxidized soybean oil	*ca.* 1,000	1.10
	Others		
DOTP	Di(2-ethylhexyl) terephthalate	390	1.03
DINCH	Di(isononyl) cyclohexane-1, 2-dicarboxylic acid ester	422	1.09
DOZ	Di(2-ethylhexyl) azelate	412	1.02

[a] Substitution factor = parts per 100 of resin (phr) required for 80A Durometer hardness at room temperature vs. required DOP level (52.9 phr).

Table 7.1. The SF reported is a comparison of the plasticizing efficiency of each plasticizer relative to DOP, and is used to determine the concentration required to achieve 70 Durometer A hardness.

The SFs enable the formulator to readily approximate the needed formulation changes, as the effects of different plasticizers are considered. For example, to compare equal Shore A 82 hardness formulations for four common plasticizers—DOP, DINP, DIDP (diisodecyl phthalate), and DOTP (di-2-ethylhexyl terephthalate)—the substitution factors from Table 7.1 yield the following equal hardness formulations:

	DOP	DINP	DIDP	DOTP
SF	1.00	1.06	1.10	1.03
PVC resin (parts)	100	100	100	100
Plasticizer (phr)	50	53	55	51.5
Stabilizer (phr)	2.0	2.0	2.0	2.0
Stearic acid (phr)	0.3	0.3	0.3	0.3

Diisononyl adipate (DINA) and dinonyl phthalate (L9P) are very similar to DOP with respect to plasticizing efficiency as measured by Durometer hardness. This is verified in the data tables showing performance comparisons of the various plasticizers. Figure 7.2 shows the effect of the concentration of these three plasticizers and that of DINP on the brittleness temperature as measured by ASTM D-746. In this plot, the low-temperature plasticizers L9P and DINA are distinctly different from that observed for DINP and DOP, which are similar to one another.

By combining the data from Fig. 7.2 with known Shore A hardness versus plasticizer relationships as illustrated in Fig. 7.1, it is possible to predict the effect of substituting the adjusted level of these plasticizers on low-temperature brittleness. This relationship is shown in Fig. 7.3. The net effects are that when formulated at adjusted concentrations (using SF) to provide equivalent PVC hardness, the DINP-plasticized

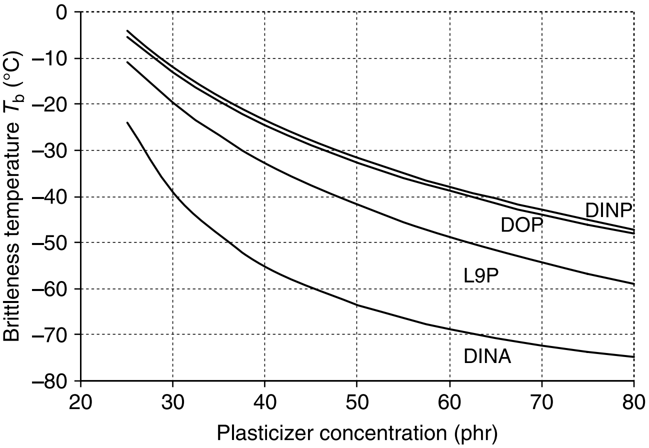

Figure 7.2 Brittleness versus plasticizer concentration.

PVC has slightly better-low-temperature brittleness than does the DOP-plasticized PVC. At equivalent Shore A 70 hardness, L9P and DINA give improvements in brittleness temperature by about −10 and −28 °C, respectively, versus DOP. As Fig. 7.3 also suggests, the low-temperature brittleness of DINA blends with any of the phthalates will fall in the expected intermediate ranges, as a function of the plasticizer blend composition.

In the comparisons that follow, equal efficiency levels are based on Durometer A hardness. Equal phr levels are also shown at 50 phr, since much of the literature uses this type of comparison. However, for most applications, it is the equal-hardness or equal-efficiency comparison that provides the most useful performance and economic basis.

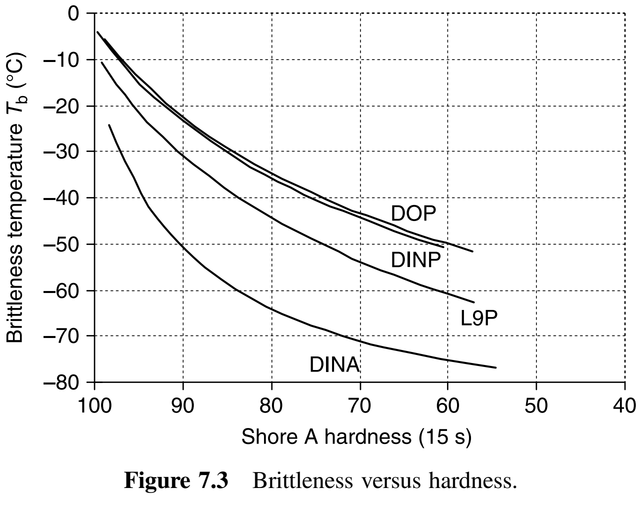

Figure 7.3 Brittleness versus hardness.

Except where shown, the following basic formulations were used in determining the performance of the plasticizers outlined in this section:

	Compound	Plastisol
PVC (suspension grade, K 69) (parts)	100	—
PVC (dispersion grade, K 74) (parts)	—	100
Plasticizer (phr)	25, 35, 50	50, 70, 90
Ba/Cd/Zn liquid stabilizer (phr)	2.0	2.0
Stearic acid (phr)	0.25	—

Performance properties were measured on these six test formulations for each plasticizer shown, and data were fitted to a smoothed curve by means of least-squares analyses. The Durometer A 70 hardness data were obtained through analyses and extrapolations of this data.

7.4.1 General Purpose Plasticizers

Approximately 60 percent of flexible PVC products utilize what are considered general purpose (GP) plasticizers. The description *general purpose* is used to describe plasticizers that can be used in a variety of applications, offering balanced properties, usually at the lowest costs. GP plasticizers are presently limited to the phthalate esters prepared from the lower-cost branched-chain alcohols, ranging from isoheptanol to isononanol. General purpose performance can also be obtained through blends of phthalate esters such as a C_7 phthalate or C_8 phthalate with a higher-performing plasticizer such as diisononyl phthalate (DINP) or diisodecyl phthalate (DIDP). Blends such as these have been available for many years; current examples include Jayflex® 251 and Palatinol® 7PHP.

Phthalate esters of straight-chain (normal) alcohols and linear alcohols are generally available as ester blends, with an averaging carbon number of the alcohol about C_8 to C_9. These types of linear phthalates offer excellent performance, in some applications, often with advantaged processing characteristics, and are used in a variety of products. However, these linear plasticizers are more costly than the branched-chain counterparts. Accordingly, the linear phthalates are generally used for specific performance qualities not attainable with GP phthalates (unless augmented with premium secondary plasticizers). Examples of these linear plasticizers include di-n-$C_6C_8C_{10}$ phthalate (610P prepared from a mixture of C_6, C_8, and C_{10} straight-chain alcohols) and the linear C_9, C_7C_9, $C_7C_9C_{11}$, and C_{11} phthalates. The price premium on these straight-chain/linear phthalates then from being usable as GP plasticizers.

There can be differences in the processability, performance and cost of compounds based on GP plasticizers described in this section. A typical Shore

A 80 hardness formulation, with a specific gravity of 1.29, based on GP plasticizers might be:

PVC (K68)	100 parts
DINP	55
ESO	3
Ba/Zn stabilizer	2.5
$CaCO_3$	20
Stearic acid	0.25
Pigments	3–10

Di-2-ethylhexyl Phthalate (DOP) and Diisooctyl Phthalate (DIOP) DOP is considered the industry standard GP plasticizer by virtue of its more than 65 years of use, its widespread use in a number of applications world wide and the good balance of properties it imparts in less demanding applications. It is sanctioned by the U.S. FDA and similar organizations in many other countries for a number of food-packaging applications. It also has a long history of safe usage in medical devices and tubing. For many years, DOP was the number one plasticizer choice; today DOP remains the most important plasticizer in the Asia–Pacific region, while in both North America and Western Europe, this lead has been overtaken by DINP. The other important C_8 phthalate ester, DIOP, is generally considered interchangeable with DOP in many applications. However, FDA sanctions are somewhat narrower for DIOP, and its use in medical applications is limited. Another related C_8 phthalate ester is dicapryl ester (DCP). DCP is especially interesting for use in plastisols by virtue of the low plastisol viscosity it imparts. Because it is based on a limited supply of capryl alcohol, a by-product of sebacic acid manufacture, its use is limited.

Diisoheptyl Phthalate (DIHP) This plasticizer is stronger solvating or faster fusing properties than both DOP and DIOP, but is more volatile. It is used in applications where faster gelation, quicker processing, or lower fusion temperatures are required. It is often used in mixtures with DINP or DIDP to help balance performance and processability for various applications. DIHP is used in carpet backing, resilient flooring, rotomolded articles, and automotive underbody coatings.

Di-2-ethylhexyl Terephthalate (DOTP) and Di-2-ethylhexyl Isophthalate (DOIP) Although the chemical structures of these two aromatic esters are very similar to the phthalate ester DOP, these plasticizers differ slightly in performance properties. This is especially true with DOTP, which imparts better low-temperature properties, lower volatility, and lower plastisol viscosity versus DOP. However, it is less compatible, especially when secondary plasticizers are incorporated into the product. The plasticizing efficiency and volatility of DOTP are similar to those of DINP. DOTP finds some use especially in plastisol applications, lower-temperature-rated wire compounds, calendered films, and gaskets. For applications with mar resistance requirements, DOTP offers superior performance over other phthalates. Eastman has recently renamed their DOTP from Kodaflex® DOTP to Eastman® 168 Plasticizer, and is now describing DOTP as an orthophthalate-free plasticizer. To offset the deficiencies of DOTP in gelation temperature, DOTP is also available in a blend with a benzoate ester; this product is offered as Eastman® 425.

The performance of DOIP is intermediate between those of DOP and DOTP, as might be expected. Commercial usage of DOIP is limited primarily because of the cost competitiveness versus DOP and DINP.

The performance comparison of the C7 and C8 phthalates and DOTP are shown in Table 7.2.

Branched C_9 Phthalates: Slightly Branched ("SLBR") DINP; Moderately Branched ("MODBR") DINP; Highly Branched ("HIBR") DINP There are three types of C_9 branched-chain phthalate esters that have been commercially available in some form for over 50 years. All three DINP esters are made with branched C_9 alcohols produced through the hydroformylation or OXO process, with the difference in alcohol branching arising from the choice of C_8 olefin feed. The SLBR C_9 alcohols are prepared from hydroformylation of an octene feed based on the dimerization of n-butenes. Here, the nonyl groups have primarily monomethyl- and dimethyl-substituted backbones, yielding a C_9 phthalate ester with a low level of branching, usually on the order of about 1.3–1.7 (average) methyl branches per C_9 alcohol structure. The C_9 alcohol used in MODBR DINP is based on branched olefins made from mixed C_3 to C_5 olefin feeds. This results in nonyl groups that have primarily disubstituted backbones. The degree of branching for MODBR DINP is about 1.8–2.1 (average) methyl branches per alcohol. The third type of DINP is prepared from a C_9 alcohol based on diisobutylene; hydroformylation of this type of octene yields the highly branched C_9 alcohol 3,5,5-trimethyl hexanol (3 methyl branches per alcohol). Although this type of DINP was the first OXO-based C_9 phthalate ester to be commercially available, it has all but disappeared from use due to its reduced plasticizing efficiency, poor low-temperature flexibility, and higher volatility compared with the other two types of DINPs.

Investigations of structural effects (degree of branching) with C_9 phthalates show that less branched isomers offer improved plasticizing efficiency, low-temperature flexibility, and volatilization properties.[8,9] Increased branching offers improvements in both electrical volume resistivity and plastisol viscosity stability. The location and number of methyl branches also impact performance properties. For example, the phthalate ester of 2-methyl-1-octanol is only slightly different from the performance of di-n-nonyl phthalate. Both the SLBR and MODBR types of DINPs find use in a variety of applications, including, wire and cable jacketing, low-temperature wire insulation, flooring, automotive underbody sealants, calendered film, coated fabrics, extruded products, shoe soles, furniture, wall coverings, and gloves. Table 7.3 shows PVC performance characteristics of GP C_9 phthalates, as well as that of the linear phthalate L9P.

TABLE 7.2 Performance Comparisons of the C_7 and C_8 Phthalate GP Plasticizers in PVC at 50 phr and 70A Hardness[7]

Parameter	DIHP		DIOP		DOP		DOTP	
Plasticizer (phr)	50	66.2	50	69.6	50	68.6	50	70.9
Substitution factor SF	—	0.97	—	1.01	—	1.00	—	1.03
Specific gravity, 20/20 °C	1.23	1.21	1.23	1.19	1.23	1.20	1.23	1.19
Shore A hardness, 15 s	80.6	70	82.4	70	81.9	70	82.9	70
Modulus at 100% elongation:								
psi	1460	980	1790	1050	1720	1040	1880	1140
kg/cm^2	103	69	126	74	121	73	132	80
Tensile strength:								
psi	2940	2420	2950	2330	2980	2430	3080	2520
kg/cm^2	207	170	207	164	209	171	217	177
Ultimate elongation (%)	338	373	334	374	328	365	349	390
Low-temperature property (°C):								
Clash–Berg[a], T_f	−23.6	−37.5	−23.8	−40.0	−24.9	−39.8	−27.7	−43.8
Brittleness[b]	−32.3	−42.1	−30.0	−42.3	−32.9	−43.5	−33.4	−45.4
Weight loss[c] (%)	19.1	22.2	10.3	15.1	10.6	15.3	7.0	7.6

[a] ASTM D 1043, T_f at 135,000 psi.

[b] ASTM D 746.

[c] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

TABLE 7.3 Performance Comparisons of C_9 Phthalate Esters in PVC at 50 phr and 70A Hardness[7]

Parameter	DINP (MODBR)		DINP (SLBR)		L9P (linear)	
Plasticizer (phr)	50	73.0	50	71.0	50	68.6
Substitution factor SF	—	1.06	—	1.04	—	1.00
Specific gravity, 20/20 °C	1.22	1.18	1.22	1.19	1.22	1.19
Shore A hardness, 15 s	83.8	70	83.0	70	82.0	70
Modulus at 100% elongation:						
psi	1820	1020	1710	1000	1610	950
kg/cm^2	128	72	120	70	113	67
Tensile strength:						
psi	2980	2320	3040	2400	2920	2340
kg/cm^2	209	163	214	169	205	165
Ultimate elongation (%)	329	366	365	404	345	377
Low-temperature properties (°C):						
Clash–Berg[a], T_f	−23.6	−41.0	−25.8	−42.6	−34.3	−49.9
Brittleness[b]	−31.8	−44.5	−35.2	−47.5	−41.4	−53.7
Weight loss[c] (%)	5.4	6.2	4.0	4.5	3.7	3.7

[a] ASTM D 1043, T_f at 135,000 psi.

[b] ASTM D 746.

[c] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

7.4.2 Strong-Solvating Plasticizers

In some processing operations, there may be a need to accomplish the gelation or fusion stages at lower temperatures than can be achieved with GP plasticizers. One way to resolve this problem is by changing to a PVC resin with a lower *K*-value or to use a copolymer resin. Frequently, the use of a strong solvating plasticizer as a partial or as a complete replacement for the GP plasticizer is practiced. Generally, the strong solvating plasticizers are more volatile and higher priced than the GP plasticizers, which must be considered in light of performance requirements. The strong solvators tend to give improved stain resistance, particularly in vinyl flooring compositions, and for this reason they are widely used in vinyl flooring. Some of the stain resistance is attributed to a closer match of solubility parameters of the plasticizer and the PVC. It is also partially due to higher volatility of these plasticizers, since plasticizers lost in processing can lead to "case-hardening"[10] on the vinyl surface. Strong-solvating plasticizers include lower-molecular-weight phthalates and benzoates, and are discussed in the following sections.

7.4.2.1 *Phthalates*

Butyl Benzyl Phthalate (BBP) This is sometimes considered the industry standard for strong-solvating plasticizers for PVC. Contrary to the various BOPs, BBP is a true co-ester because it is made by a special process using benzyl chloride in place of benzyl alcohol.[11] It has a favorable balance of solvation rate and volatility, but suffers from poor low-temperature, heat stability, and light stability properties. In some formulations, the high specific gravity of BBP may be at an economic disadvantage for products sold on a volume cost basis. BBP has been the most widely used stain-resistant plasticizer in vinyl flooring, but its use, especially in Europe, is declining.

Diisobutyl Phthalate (DIBP) and Dibutyl Phthalate (DBP) While these are particularly strong solvators, both of them suffer from excessively high volatility. In the United States, DBP is also a component of co-ester blends such as butyl octyl phthalate (BOP). However, the use of DBP or DIBP as a primary plasticizer or as a secondary plasticizer is limited because of the higher volatility, the higher specific gravity, and the price premium. In a few countries, DIBP is priced below DOP, and there it sees a wider use in spite of the high volatility. The higher volatility is reflected in excessive fuming under vinyl processing conditions and significant stiffening of the flexible vinyl after only a short time period in use. Diamyl (or pentyl) phthalate has also been used as a strong-solvating plasticizer, but its cost and the limited supply of amyl alcohol has precluded wider use.

Di-n-hexyl Phthalate (DnHP) This phthalate ester, prepared from n-hexanol, is less solvating than DIBP and DBP, has lower volatility, and imparts better low-temperature properties. Compared with BBP, DnHP is also less solvating and is slightly more volatile, but it is more efficient and imparts better low-temperature properties. DnHP has a PVC fusion temperature of 125 °C versus 140 °C for DOP as measured in the cone-and-plate viscosity test. However, since it is significantly lower in specific gravity versus BBP, there is considerable potential for cost savings in using DnHP. DnHP also imparts improved color stability under exposure to elevated temperatures and ultraviolet energy. A similar product based on a mixture of branched and linear C_6 alcohols, DHP, has been discontinued; DnHP is reported to offer the same processing performance of DHP but with the lower-volatility advantage of a DIHP.[12]

Butyl Octyl Phthalate (BOP) Historically, there have been numerous products sold as BOP, ranging from simple blends of DBP and DOP to so-called co-esters made by co-esterification of phthalic anhydride with various mixtures of n-butanol and 2-ethylhexanol. These "co-esters" consist of DBP, DOP, and the actual co-ester, butyl octyl phthalate. As might be expected, performance covers a range of solvation rates, volatilities, and other properties, all of which fall between DBP and DOP.

Performance comparisons of strong-solvating phthalates in PVC are shown in Table 7.4.

7.4.2.2 Benzoates

Propylene Glycol Dibenzoate (PGDB), Dipropylene Glycol Dibenzoate (DPGDB), and Diethylene Glycol Dibenzoate/Dipropylene Glycol

TABLE 7.4 Performance Comparisons of Strong-Solvating Plasticizers in PVC at 50 phr and 70A Hardness[7]

Parameter	DBP		DnHP[a]		BOP[b]		BBP	
Plasticizer (phr)	50	58.7	50	66.1	50	65.3	50	64.1
Substitution factor SF	—	0.86	—	0.98	—	0.95	—	0.93
Specific gravity, 20/20 °C	1.26	1.25	1.24	1.20	1.23	1.21	1.29	1.28
Shore A hardness, 15 s	75.7	70	80.5	70	79.4	70	79.8	70
Modulus at 100% elongation:								
psi	1220	980	1470	910	1460	1000	1730	1170
kg/cm^2	86	69	103	64	103	70	122	80
Tensile strength:								
psi	2550	2420	2920	2390	2980	2450	3620	2760
kg/cm^2	179	157	205	168	210	172	255	194
Ultimate elongation (%)	317	334	335	403	341	372	309	345
Low-temperature property (°C):								
Clash–Berg[c], T_f	−23.1	−32.5	−28.2	−42.4	−26.9	−39.9	−11.0	−22.2
Brittleness[d]	−30.8	−37.6	−33.4	−45.1	−31.9	−41.1	−12.3	−22.3
Weight loss[e] (%)	25.1	31.0	18.0	21.3	16.3	22.5	15.0	20.4

[a] Data extrapolated from R. Kozlowski, "Performance of di-n-Hexyl Phthalate in Flexible Vinyl Formulations."[11,12]

[b] BOP average carbon number of 7.2.

[c] ASTM D 1043, T_f at 135,000 psi.

[d] ASTM D 746.

[e] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

Dibenzoate Blends (DEGDB/DPGDB) DPGDB has been employed in vinyl flooring products as an alternative PVC plasticizer to BBP. It is also similar in specific gravity, but has lower volatility. In addition, proprietary benzoate blends including blends other esters such as DOA or 2-ethylhexyl benzoate are available, giving more balanced price/performance acceptance. Benzoflex® 2000 is one such example. Benzoates have also been shown to improve the performance of GP plasticizers such as DINP and DOTP in a variety of applications[13] when added as a secondary plasticizer. A more complete understanding of these and other benzoate plasticizers is presented in Chapter 8.

7.4.3 Low-Temperature Plasticizers

There are basically two major types of low-temperature plasticizers: (i) phthalates of straight-chain or linear alcohols and (ii) aliphatic dibasic acid esters. Linear phthalates have been used as primary plasticizers in demanding applications such as roofing, automotive, and geomembranes. Aliphatic diesters such as DOA or DINA are more commonly used as secondary plasticizers, to improve the low-temperature performance of a primary plasticizer such as DINP or DIDP.

7.4.3.1 Linear Phthalates These are all based on straight-chain alcohols or linear alcohols. Most are based on mixed-carbon-number alcohols due to the added expense of separating the alcohols in the manufacturing process. Carbon number averages are approximately C_8, C_9, and C_{10}. There are also individual-carbon-number linear phthalates such as C_7 (L7P), C_9 (L9P), and C_{11} (DUP or L11P) phthalates. In this discussion, "linear" refers to the alcohols prepared by the hydroformylation of linear olefins. These materials are typically 50–80 percent straight chain, generally an odd carbon number in length, and the balance made up of branched alcohols substituted at the C-2 position.[14] Straight-chain alcohols are usually even carbon numbers in length and contain over 95 percent normal alcohols. Linear $C_7C_8C_9$ OXO alcohol-based plasticizers were first produced in the United Kingdom in the 1950s and sold on the market as di-*alphanol* phthalate (DAP); production of similar linear OXO alcohols and plasticizers began in the United States in 1970 with the introduction of Monsanto's Santicizer® 711. In the early 1960s, synthetic straight-chain alcohols of even carbon numbers became available by the ethylene chain growth process[15] and the 610P and 810P products appeared on the market shortly afterwards. In general, performance properties of straight-chain alkyl phthalates are just slightly different from those of linear phthalates.

Di-n-octyl Phthalate (DNOP) and Di-linear Heptyl Nonyl Phthalate (79P) These C_8 or C_8 average phthalates would be in the GP category except for price. Their performance is superior to that of DOP in some respects, especially their balance of solvating strength, low-temperature flexibility, and low volatility. Fusco et al.[16] in their reporting of the performance of DnOP versus DOP, showed that although both plasticizers yielded equivalent hardness, DnOP had an advantaged low temperature performance of 9 °C in the Clash–Berg test and offered a reduction in volatile losses by almost 70 percent. Today, DnOP is rarely seen as a plasticizer product of commerce; DnOP is however, one of several components in 610P and 810P.

The performance of diheptyl phthalate is similar to that of DOP, with equivalent efficiency. It also offers advantages over DOP in reduced volatility and in low-temperature flexibility, but the advantages cited are not as great as those seen for DnOP. The efficiency of L79P, made from a mixture of linear C_7 to C_9 OXO alcohols, is equivalent to that of DOP. L79P does offer advantages of improved low-temperature flexibility and processability.

Di-n-$C_6C_8C_{10}$ Phthalate (610P), Di-Linear $C_7C_9C_{11}$ Phthalate (711P), Di-Linear C_9 Phthalate (L9P), Di-n-C_8C_{10} Phthalate (810P), and Phthalate/Adipate Blends As is the case with C_8 or C_8 average normal and linear phthalates, the C_9 average linear phthalate mixtures would also be GP plasticizers except for cost. Although these plasticizers are less volatile and give slightly better low-temperature properties than do L79P and DNOP, they are also slightly less solvating.

The combination of good low-temperature performance, low volatility, and improved resistance to UV exposure was responsible in the 1970s for the use of these plasticizers to replace of DOP/DOA blends in applications such as automotive upholstery, PVC roofing, geomembranes, and pool liners. It is possible to equal both the low-temperature and volatility performance of the C_8 and C_9 straight-chain/linear phthalates by using blends of C_9 or C_{10} branched alkyl phthalates and adipate esters such as DOA or DINA. In fact, these blends are important whenever the price differential between straight-chain/linear phthalates and branched-chain phthalates increases. For example, an 85/15 weight percent blend of DIDP/DINA provides equivalent hardness and low-temperature properties with about 40 percent lower volatility than 711P when substituted at 1.10 SF versus the 711P. Performance comparisons of C_9 average linear phthalates, L9P, and a blend of a branched-chain phthalate/adipate ester are shown in Table 7.5.

The plasticizers 610P and 711P are phthalate coesters of mixed alcohols (normal or straight-chain $C_6C_8C_{10}$ alcohols and linear $C_7C_9C_{11}$ alcohols, respectively), with the average carbon number being about 9 for both products. Table 7.5 shows that these two plasticizers and L9P are very similar in plasticizing efficiency (as measured by hardness) and are significantly more efficient than DINP. Volatile losses after 7 days at 100 °C are similar for 610P and 711P; these plasticizers suffer from high-volatility losses attributed to the presence of lower-molecular-weight esters based on C_6 and C_7 alcohols. The volatility impact of these lower-carbon-number esters is evident in comparisons with the performance of the plasticizer L9P; here, L9P offers lower volatility and greater permanence and a slight improvement in low-temperature flexibility.

Low-temperature properties of 610P are about 1–2 °C better than 711P (at about 40 phr plasticizer), due to being based on over 99 percent straight-chain alcohols. All three of these low-temperature phthalates impart about 6–9 °C better low-temperature properties than the DINPs at equal hardness. The phthalate ester 810P is made from a blend of C_8 and C_{10} straight chain alcohols. Because of its greater resistance to UV

TABLE 7.5 Performance Comparisons of Linear Phthalates and a Phthalate/Adipate Blend in PVC at 50 phr and 70A Hardness[7]

Parameter	610P		711P		L9P		DIDP/DINA (85/15)	
Plasticizer (phr)	50	67.5	50	67.5	50	68.6	50	74.1
Substitution factor SF	—	0.98	—	0.98	—	1.00	—	1.08
Specific gravity, 20/20 °C	1.22	1.19	1.22	1.19	1.22	1.19	1.21	1.17
Shore A hardness, 15 s	81.7	70	81.5	70	82.0	70	84.8	70
Modulus at 100% elongation:								
psi	1520	1040	1720	1070	1610	950	1830	1010
kg/cm^2	107	73	121	75	113	67	129	71
Tensile strength:								
psi	2800	2320	2950	2390	2920	2340	3040	2310
kg/cm^2	197	163	208	168	205	165	214	163
Ultimate elongation (%)	314	346	342	373	345	377	354	421
Low-temperature property (°C):								
Clash–Berg[a], T_f	−33.5	−48.7	−32.0	−47.2	−34.3	−49.9	−29.9	−49.2
Brittleness[b]	−41.5	−52.6	−40.6	−51.2	−41.4	−53.7	−38.0	−51.9
Weight loss[c] (%)	4.5	5.7	5.6	6.5	3.3	3.7	3.1	4.0

[a] ASTM D 1043, T_f at 135,000 psi.

[b] ASTM D 746.

[c] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

aging and discoloration, combined with lower volatility, it is used in PVC roofing membranes, low-fogging automotive interior products, and low-temperature wire and cable applications. Of this series of linear phthalates, L9P has the best balance of plasticizing efficiency, low-temperature properties and volatility characteristics.

The phthalate/adipate blend of Table 7.5 is less efficient than the straight-chain and linear phthalates, and is deficient in low-temperature properties when compared at equal phr. At equivalent hardness, however, the low-temperature properties are essentially the same as the straight-chain and linear phthalates. The DIDP blend with DINA does offer the lowest volatility of this series.

7.4.3.2 Aliphatic Dibasic Acid Esters These types of plasticizing esters are based on aliphatic dibasic acids with carbon numbers ranging from C_5 (glutaric) to C_{10} (sebacic), with adipate esters by far the most important in this group of plasticizers. These esters are generally used as secondary plasticizers to augment the low-temperature performance of GP phthalates or to reduce the viscosity of plastisols. They may be used as primary plasticizers in clear PVC film for meat and produce wrap, gaskets intended for cold weather applications, and in flexible vinyl strips used in cold-room doors.

Diisooctyl Adipate (DIOA), Di-2-ethylhexyl Adipate (DOA), and Di-linear C_7C_9 Adipate (79A) Of this group of C_8 (or C_8 average) adipates, DOA is by far the most widely used. It has a long history of use in meat wrap due to the high oxygen transfer and the good low-temperature properties that it imparts. DIOA performance is essentially the same as that of DOA, but it is less widely used. The plasticizer 79A imparts a better balance of low-temperature flexibility and volatility than does DOA and has also been used in clear blown film for meat and produce wrap. However, higher prices compared with DOA have limited the applications of DIOA and 79A to a few specialized areas.

Diisononyl Adipate (DINA) This ester is considerably less volatile than DOA and DIOA. Although it can be used alone as primary plasticizer in flexible PVC meat wrap, its major uses are as secondary plasticizer blends with DINP and DIDP, to improve the overall low-temperature performance. Plasticizing efficiency, however, is significantly less than that of the C_8 adipates, thereby limiting its use as a primary plasticizer.

n-Octyl n-Decyl Adipate (NODA) While imparting better low-temperature flexibility and lower volatility than DINA, the substantial premium for this ester limits its use. It has, however, been used occasionally in PVC food wrap films.

Diisodecyl Adipate (DIDA), Di-2-ethylhexyl Azelate (DOZ), Di-2-ethylhexyl Sebacate (DOS), and Diisodecyl Glutarate (DIDG) These esters are not extensively used in flexible PVC, because they offer less than optimum performance with respect to cost and compatibility. In general, the family of aliphatic dibasic acid esters ranges in total carbon number from C_{18} to C_{26}. Those of low carbon number are excessively volatile, while those of high carbon number are limited in compatibility with PVC.

Comparisons of the performance of the more commonly used aliphatic dibasic acid esters are shown in Table 7.6. The following is an example of a 82 Shore A hardness GP-type starting formulation that is modified for low-temperature flexibility:

PVC (suspension grade, K 68)	100
DINP	45
DINA	7
ESO	3
Ba/Zn stabilizer	2.5
Stearic acid	0.25
Pigments	0–10 as needed

Here the addition of 7 phr DINA to the formula will increase the lower temperature limit as reported by the Clash–Berg T_f method by almost 10 °C over the same formulation without DINA.

7.4.4 Low-Volatility Plasticizers

The plasticizers in this category cover a range of volatilities from significantly lower than the GP phthalates to those with volatility losses comparable to those observed with polymeric plasticizers. The overall performance of these low-volatility monomeric plasticizers differs considerably from the polymerics. Compared with most polymerics, these low-volatility plasticizers are easier to handle, impart much better low-temperature properties, are more efficient, are lower in specific gravity, and offer better resistance to aqueous extraction. Thus, even if priced comparably to a polymeric, the high plasticizing efficiency and low specific gravity of monomeric plasticizers can contribute to overall lower compound costs. It is important to note that poorer or reduced plasticizer efficiency helps to lower the volume cost of GP compounds; but as cost of plasticizers rises, especially in situations where there are declining PVC resin prices, there is a point where poorer efficiency contributes to higher formulation compound costs.

7.4.4.1 Phthalates These are the most economical low-volatility plasticizers. Compatibility constraints limit attempts to reduce volatility by increased phthalate molecular weight, with the practical upper limit being the C_{13} branched-chain phthalate ester DTDP. Phthalate esters prepared with C_{14} and higher-molecular-weight alcohols are not compatible with PVC.

Diisodecyl Phthalate (DIDP) and Di-2-propylheptyl Phthalate (DPHP) The most commonly used low-volatility plasticizer available worldwide is DIDP. DIDP has been used as a permanent plasticizer for more than 50 years, first being produced commercially in 1954 from isodecanol produced via the OXO process. It has found

TABLE 7.6 Performance Comparisons of Low-Temperature Aliphatic Dicarboxylic Acid Esters in PVC at 50 phr and 70A Hardness[7]

Parameter	DOA		DIOA		DINA		DOZ	
Plasticizer (phr)	50	63.5	50	65.0	50	69.5	50	70.2
Substitution factor SF	—	0.93	—	0.95	—	1.01	—	1.02
Specific gravity, 20/20 °C	1.20	1.17	1.20	1.17	1.20	1.16	1.19	1.15
Shore A hardness, 15 s	78.5	70	79.6	70	80.6	70	82.0	70
Modulus at 100% elongation:								
psi	1200	850	1410	1050	1430	990	1870	1210
kg/cm^2	84	60	99	74	101	70	132	85
Tensile strength:								
psi	2740	2270	2670	2300	2750	2230	2880	2260
kg/cm^2	193	160	188	162	194	157	203	159
Ultimate elongation (%)	365	391	339	370	349	380	323	353
Low-temperature property (°C):								
Clash–Berg[a], T_f	−53.3	−66.4	−49.8	−62.9	−50.5	−65.9	−53.6	−71.9
Brittleness[b]	−62.7	−68.7	−62.4	−70.9	−63.8	−71.3	−65.7	−78.0
Weight loss[c] (%)	27.5	33.0	23.3	30.3	9.2	11.3	9.5	10.6

[a] ASTM D 1043, T_f at 135,000 psi.

[b] ASTM D 746.

[c] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

utility in a number of wire and cable applications, geomembranes, tarpaulins, automotive interiors, and other applications where the volatility of GP plasticizers does not meet the requirements. DIDP is also approved by the FDA for several food packaging applications. Another C_{10} phthalate ester plasticizer has recently been reintroduced to the plasticizer community: DPHP.[17] The performance of this branched C_{10} phthalate ester is similar to that of DIDP, although it does exhibit higher volatile losses and requires slightly higher processing temperatures. Both products have similar efficiency and similar low-temperature performance, but in unfilled products without UV stabilizers, DPHP does offer some improvement in resistance to yellowing.

Di-linear C_9C_{11} Phthalate (911P), Diundecyl Phthalate (DUP or L11P) There are several versions of the linear C_9C_{11} phthalate ester, where the composition differs slightly based on the source of alcohol. Some 911P plasticizers are prepared form an alcohol feed with about equal proportions of C_9 and C_{11} alcohols; others are C_{11}-rich; while yet other plasticizers are based on a mixture of C_9, C_{10}, and C_{11} alcohols. While there is a significant advantage in terms of volatility and low-temperature performance for 911P in comparison with DIDP and DPHP, it comes with a high price premium. DUP or L11P is based on a linear C_{11} alcohol and imparts superior low-temperature flexibility and low volatility over both 911P and DIDP.

Diiso $C_{11}C_{12}C_{13}$ Phthalate (UDP), and Ditridecyl Phthalate (DTDP) The volatilities of these high-molecular-weight plasticizers are intermediate to those of 911P and the trimellitates. DUP is superior to UDP in volatility and is slightly more volatile than DTDP. DUP also imparts far superior low-temperature flexibility compared with both UDP and DTDP.

Comparisons of the performance of low-volatility phthalates are shown in Table 7.7.

7.4.4.2 Trimellitates Except for a very few highly specialized and expensive esters, the trimellitate ester plasticizers currently represent the state of the art in low-volatility monomeric plasticizers. As in the case with phthalates, the branched-chain trimellitate esters are less expensive than the straight-chain/linear trimellitates. Linear trimellitates offer improved low-temperature flexibility and processability over their branched counterparts.

Trimellitate esters were first introduced in the late 1960s. These plasticizers rapidly gained acceptance in higher-temperature PVC wire insulation. The lower migration rates of trimellitates have created additional demand for these products in gaskets.[19]

Tri-2-ethylhexyl Trimellitate (TOTM), Triisooctyl Trimellitate (TIOTM), and Triisononyl Trimellitate (TINTM) TIOTM and TOTM are considered interchangeable by many formulators, as they yield very similar performances. TINTM is significantly less volatile than the C_8 esters. It does impart better low-temperature flexibility, when formulated at adjusted efficiency. However, because of its higher viscosity, it is more difficult to dry-blend and process.

TABLE 7.7 Performance Comparisons of Low-Volatility Plasticizers in PVC at 50 phr and 70A Hardness[7]

Parameter	DIDP		DPHP[a]		DUP (L11P)		911P		DTDP	
Plasticizer (phr)	50	75.8	50	76.7	50	78.4	50	72.5	50	86.5
Substitution factor SF	—	1.10	—	1.10	—	1.14	—	1.06	—	1.26
Specific gravity, 20/20 °C	1.22	1.17	1.22	1.17	1.21	1.16	1.22	1.18	1.21	1.15
Shore A hardness, 15 s	85.6	70	86.0	70	86.3	70	83.4	70	89.5	70
Modulus at 100% elongation:										
psi	1890	1010	1870	940	1820	890	1840	1110	1940	720
kg/cm^2	133	71	132	66	128	63	129	78	136	51
Tensile strength:										
psi	2990	2250	2990	2300	2830	1910	2860	2210	3050	2080
kg/cm^2	210	158	210	162	199	134	201	155	214	146
Ultimate elongation (%)	327	361	310	370	310	331	294	324	324	398
Low-temperature property (°C):										
Clash–Berg[b], T_f	−23.6	−42.7	−24.5	−44.5	−34.3	−56.6	−34.3	−52.3	−24.2	−50.4
Brittleness[c]	−31.8	−46.2	−30.7	−42.8	−46.6	−64.3	−43.4	−57.4	−31.5	−52.4
Weight loss[d] (%)	3.0	3.8	3.6	4.7	1.5	2.0	2.2	2.6	1.9	1.9

[a] A. D. Godwin.[18]

[b] ASTM D 1043, T_f at 135,000 psi.

[c] ASTM D 746.

[d] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

Tri-n-C_6C_8 Trimellitate (NHOTM) and Tri-n-C_8C_{10} Trimellitate (NODTM) These esters cover a range of performance in terms of solvency, low-temperature properties, and volatility. NHOTM is faster-solvating and imparts better low-temperature properties than do the foregoing branched-chain trimellitates, although it is somewhat more volatile. NODTM has the lowest volatility of all the trimellitates and also the best low-temperature properties. However, both of these straight-chain esters are significantly more expensive than the branched-chain trimellitates.

Comparisons of the performance of the trimellitates are shown in Table 7.8.

7.4.4.3 Other Low-Volatility Monomeric Plasticizers Aside from phthalates, trimellitates, and epoxidized oils, the only other low-volatility monomeric-type plasticizers currently available are shorter-chain fatty acid esters of pentaerythritol (PE) and dipentaerythritol (DPE). The PE ester is in the molecular weight range of the trimellitates and DTDP and thus has comparable volatility to these types of plasticizers. The DPE ester (actually a blend of PE and DPE esters) approaches the higher-molecular-weight range of the epoxidized oils. Both of these products are characterized by low viscosity.

7.4.5 Other Plasticizers

There are numerous highly specialized plasticizers used in PVC formulating. With the exception of certain chlorinated hydrocarbons and most hydrocarbon extender types, these plasticizers generally command a significant price premium. They are used by virtue of their unique performance in processing or end-use properties.

2,2,4-Trimethyl-1,3-pentanediol Diisobutyrate (TXIB) This volatile plasticizer is highly effective in the viscosity reduction of in plastisols and finds utility in a number of different applications. It also imparts improved stain resistance to vinyl flooring, in part due to its high volatility and compatibility.

2,2,4-Trimethyl-1,3-pentanediol Isobutyrate Benzoate The outstanding characteristic of this plasticizer is the stain resistance that it imparts in vinyl flooring applications. However, it is also quite volatile and imparts poor low-temperature properties.

2,2,4-Trimethyl-1,3-pentanediol Monoisobutyrate Benzyl Phthalate This ester is a strong solvator; but, unlike most strong solvating carboxylic acid esters, it is relatively low in volatility. It is also quite inefficient and imparts poorer low-temperature properties. It has become an important plasticizer for “paint-compatible” automotive undercoatings, due to its high surface tension and for plastisol inks because of its low plasticizer migration rates.

Alkyl Sulfonic Acid Esters of Phenol There are two esters in this category, differing in average chain length of the alkyl group. The esters are reported to be used for GP applications in Europe and are often promoted as a phthalate alternative. They are also used in polyurethane sealants. Plasticizing efficiency (SF) is similar to that of

TABLE 7.8 Performance Comparisons of Trimellitate Ester Plasticizers in PVC at 50 phr and 70A Hardness [7]

Parameter	TOTM		TIOTM		TINTM		NODTM (810TM)	
Plasticizer (phr)	50	76.1	50	80.3	50	85.3	50	73.9
Substitution factor SF	—	1.11	—	1.17	—	1.24	—	1.08
Specific gravity, 20/20 °C	1.23	1.19	1.23	1.18	1.22	1.17	1.22	1.18
Shore A hardness, 15 s	86.5	70	87.8	70	89.7	70	85.3	70
Modulus at 100% elongation:								
psi	1990	1110	2120	1050	2170	1020	1930	1140
kg/cm^2	140	78	149	74	153	72	136	80
Tensile strength:								
psi	3040	2370	2920	2350	3010	2220	2990	2350
kg/cm^2	214	167	205	165	212	148	210	165
Ultimate elongation (%)	322	365	303	393	308	340	335	365
Low-temperature property (°C):								
Clash–Berg[a], T_f	−19.2	−39.6	−15.9	−38.6	−19.2	−45.1	−29.4	−50.5
Brittleness[b]	−33.6	−44.2	−28.6	−41.2	−32.8	−45.8	−41.5	−54.0

[a] ASTM D 1043, T_f at 135,000 psi.

[b] ASTM D 746.

DOP, but low-temperature brittleness is defective by about 5–8 °C (at 40 phr). Their outstanding characteristic is chemical resistance, especially alkali resistance. Care must be taken in storage of these esters (time, temperature, and materials used in construction of storage tanks), since their stability is not equal to that of the phthalate esters.

Dicyclohexyl Phthalate (DCHP) This plasticizer finds very limited application in PVC hot-melt adhesives. It is a solid, quite inefficient, and it imparts poor low-temperature properties. It is usually used in combination with GP phthalates, such as DOP, to enhance melt-stage processing of polymers.

Acetyl Tributyl Citrate, Acetyl Tri-n-hexyl Citrate These esters may be used in toys, special food packaging, and medical applications. They are being promoted for flexible PVC blood bags; acetyl tributyl citrate is also reportedly used in a copolymer of vinyl chloride/vinylidene chloride for food wrap. The high price premiums for the citrate plasticizers and other problems have limited the broad acceptance of citrate plasticizers in commercial flexible PVC products. PVC performance characteristics of the citrate esters are reported in Table 7.9. Higher-molecular-weight citrates

TABLE 7.9 Performance Comparisons of Citrate Ester Plasticizers in PVC at 50 phr [7,21]

Parameter	DOP	DOA	A-4[a]	A-6[a]	B-6[a]
Hardness, Durometer A, 10 s	79	78	78	81	81
Modulus at 100% elongation (psi)	1368	1092	1348	1574	1362
Tensile strength (psi)	2748	1797	2862	2978	2924
Ultimate elongation (%)	395	414	400	390	427
Clash–Berg[b] T_4 at 10,000 psi (°C)	−8.4	−30.8	−7.6	−9.1	−11.9
Clash–Berg[b] T_f at 100,000 psi (°C)	−38.3	−66.5	−35.6	−41.6	−48.7
Brittle point[c] (°C)	−24.5	−56.5	−18.5	−26.0	−33.5
Volatile loss[d] in air (%)	4.8	7.1	12.1	2.6	1.7
Volatile loss[e] activated carbon (%)	3.4	7.6	7.0	1.7	1.4
Water extraction loss[f] (%)	0.7	1.5	1.2	1.9	1.7
Soapy water extraction loss[g] (%)	2.7	11.0	9.5	5.4	2.2
Oil extraction loss[h] (%)	11.4	34.7	10.9	13.8	15.7
Silica gel migration[i] (%)	12.2	23.0	17.0	4.4	3.6

[a] Citroflex® citrate esters: A-4, acetyl tributyl citrate; A-6 acetyl tri-n-hexyl citrate; B-6, butyryl tri-n-hexyl citrate.

[b] ASTM D 1043.

[c] ASTM D 746.

[d] 24 hours at 100 °C.

[e] ASTM D 1203, 24 hours at 70 °C.

[f] 10 days at 40 °C.

[g] 24 hours at 60 °C in 1 percent soap solution.

[h] 24 hours at 60 °C in ASTM No. 3 oil.

[i] 24 hours at 70 °C in 100-mesh silica.

Note: All results of volatility and extraction losses are reported as a percentage of plasticizer loss and not weight loss of the PVC compound.

have also been suggested for use in automotive interior applications.[20] Citrate plasticizers are described in further detail in Chapter 8.

Diisononylcyclohexanedioic Acid Ester (DINCH) DINCH, prepared by the hydrogenation of a SLBR type of DINP, is finding growing applications in a few environmentally sensitive applications. This is because of its favorable toxicity profile and of its status as a nonphthalate plasticizer. This hydrogenated C_9 phthalate is less compatible in PVC than DINP, showing levels of higher exudation. DINCH also requires higher fusion and processing temperature.[18] It does, however, offer benefits of improved low-temperature flexibility, reduced plastisol viscosities, and improved resistance to yellowing from UV exposures. The processing disadvantages of DINCH can be seen through fusion property data. DOP, DOTP and DINP will achieve fusion within 4 minutes at 300 °F (149 °C) under ASTM D2396-94 test conditions, while DINCH requires an excess of 17 minutes.[22]

The C_8 version of DINCH, di-2-ethylhexyl cyclohexanedioic acid ester (also called di-2-ethylhexyl hexahydrophthalate) was produced as a commercial plasticizer in the 1950s and 1960s. This C_8 product was eventually discontinued because of unfavorable costs and performance. The performance properties of DINCH versus DINP are presented in Table 7.10.

Triglyceride Plasticizers. Glycerol Di-2-ethylhexanoic Acid/Benzoic Acid Ester and Glycerol Acetylated Esters Two differing types of glycerol esters have been recently introduced as phthalate alternatives. In one form, the performance

TABLE 7.10 Performance Comparisons of C_9 Phthalate and Cyclohexanedioate Esters in PVC at 50 phr and 70A Hardness[18]

Parameter	DINP		DINCH	
Plasticizer (phr)	50	73.0	50	75.1
Substitution factor SF	—	1.06	—	1.09
Specific gravity, 20/20 °C	1.22	1.18	1.20	1.15
Shore A hardness, 15 s	83.8	70	85.1	70
Modulus at 100% elongation:				
psi	1820	1020	1710	1000
kg/cm^2	128	72	120	70
Tensile strength:				
psi	2980	2320	2960	2300
kg/cm^2	209	163	207	162
Ultimate elongation (%)	329	366	365	380
Low-temperature properties (°C):				
Clash–Berg[a], T_f	−23.6	−41.0	−27.8	−47.6
Brittleness[b]	−31.8	−44.5	−35.2	−49.5
Weight loss[c] (%)	5.4	6.2	6.1	7.3

[a] ASTM D 1043, T_f at 135,000 psi.

[b] ASTM D 746.

[c] 7 days at 100 °C (212 °F), 40 mil (1 mm) thickness.

of castor oil is improved by modifying the structure to replace some of the longer-chain acids with acetic acid. This shift to lower-molecular-weight acids improves both the compatibility and the processability of the plasticizer. This product is described as an acetylated monoglyceride derived from hydrogenated castor oil and is reported to meet the requirements for indirect food contact additives under both the European Union (EU) and FDA regulations.[23] This ester seems to offer about the same efficiency as DOP, yet with lower volatility. Because of its high manufacturing costs, the applications of this product are expected to be limited.

The second type of glycerol triester is prepared from the esterification of glycerol with a mixture of shorter-chain aliphatic acids and benzoic acid. Here, the partial replacement with benzoic acid improves both the compatibility and the processabilty of the plasticizer. The glycerol triesters formed by esterification with 2 moles of 2-ethylhexanoic acid and 1 mole of benzoic acid seem typical of those products being proposed;[24] no applications of these products are currently known.

7.4.6 Hydrocarbon Extender Plasticizers

Starting in the mid-1940s, many petroleum and coal tar fractions were offered to the plastics industries as candidate plasticizers. Most of these were poor in color, high in odor, often either highly viscous or volatile, and limited in compatibility. Generally, they were found to be unsuitable for use as plasticizers for PVC. However, a few managed to find some use as low-cost extenders where quality was not critical. Typical products that found favorable use include butylated naphthalenes, partially hydrogenated terphenyls, and alkylbenzenes. Some of these products were sufficiently compatible to permit as much as 30 percent or more replacement of the primary plasticizer (e.g., in conjunction with DIDP in 60 °C wires). The hydrocarbon plasticizers available today may be categorized as follows.

Linear Paraffins These are high-purity products with very low odor and water-white color. They are volatile and are limited in their compatibility with PVC. For example, a 50 phr DOP-formulated compound will tolerate up to about 10 percent or 5 phr of linear paraffin. With higher-molecular-weight phthalates, the compatibility limit will be slightly reduced. The high volatility, very low viscosity, and low solvency of some linear paraffins are used to advantage as viscosity depressants in plastisols and can help improve stain resistance in resilient flooring. Linear paraffins can also serve an important lubricating function in flexible PVC processing operations.

Alkylated Aromatics At present, the only products in this category are linear alkybenzenes. As is the case with the linear paraffins, they are high in purity and low in color and odor. They are less volatile and more compatible than the linear paraffins. They are also used to reduce the viscosity of plastisols. Because the viscosity of dodecylbenzene is about four times that of a C_{15} linear aliphatic hydrocarbon, it is about 25 percent less effective in reducing plastisol viscosity. Often, linear alkylbenzenes are available in blends with linear paraffins.

Naphthenic Hydrocarbons These products are refined petroleum fractions, which are usually poorer in color and odor than the linear paraffins and alkylbenzenes. They are generally used to lower cost by replacing a portion of a GP plasticizer. Because of their poor efficiency, a higher level of the (lower-cost) hydrocarbon must be used to partially replace a phthalate and maintain the same degree of flexibility of hardness. In addition, these hydrocarbons have lower specific gravity. Thus, the lower cost, reduced efficiency, and lower specific gravity combine to yield some rather significant savings when costs are calculated on a volume basis. These savings may be partially offset in calendering, where there tends to be high volatile losses during processing. Although generally less volatile than the alkybenzenes, they are nonetheless much more volatile than GP plasticizers. Depending on the use level (usually no more

TABLE 7.11 Effect of Hydrocarbon Plasticizers on Performance of PVC Plastisols [7]

Plasticizer system:[a]			
DINP-MODBR	70	63	66.5
Jayflex® 210 (naphthenic hydrocarbon)	—	7	—
Jayflex® 215 (C_{15} average linear paraffin)	—	—	3.5
Properties of Unfused Plastisols			
Brookfield viscosity[b] at 25 °C (cP):			
3 rpm	5860	4110	3660
30 rpm	3910	3060	2590
Severs viscosity[c] at 38 °C (P):			
Shear rate 500 s^{-1}	29	19	18
Shear rate 2000 s^{-1}	45	25	24
Air release[d] (s)	104	69	78
Fusion volatility[e] (wt%)	1.4	3.0	3.0
Hot-bench gelation temperature (°C)	106	109	111
Properties of Fused/Molded Plastisols			
Shore A hardness, 15 s	71.4	73.3	72.8
Modulus at 100% elongation (psi)	1050	1180	1080
Tensile strength (psi)	2560	2420	2540
Elongation (%)	390	380	385
Low-temperature properties (°C):			
Clash–Berg[f], T_f	−39	−44	−43
Brittleness[g]	−44	−49	−46
Weight loss[h] (%)	6.5	10.2	8.1

[a] Formulation: PVC (Geon® 121), 100; plasticizer, 70; Ba–Cd–Zn stabilizer, 2.

[b] Aged 2 hours at 25 °C.

[c] Aged 4 hours at 38 °C and run at 38 °C.

[d] Huff ring, 3/8 in (9.5 mm)-diameter hole, 25 °C.

[e] Determined on plastisol samples exposed 6 min at 186 °C in forced-air oven.

[f] ASTM D 1043, T_f at 135,000 psi.

[g] ASTM D 746.

[h] Tensile bars, 40 mil (1 mm) thick; aged 7 days at 100 °C in forced-air oven.

than a maximum of 10–15 percent of the primary plasticizer, due to compatibility and volatility limitations), there will be a slight to very significant loss in performance due to this higher volatility.

The effect on performance in PVC plastisols resulting from replacing a portion of a primary plasticizer (DINP) with these plasticizers is shown in Table 7.11. The naphthenic hydrocarbon product is only about one-half as effective as the C_{15} linear aliphatic hydrocarbon with respect to reduction of plastisol viscosity.

7.5 APPLICATION AREAS

Monomeric plasticizers are used in a very broad range of applications—from barely plasticized (e.g., 25 phr) furniture wood grain laminating films, to ordinary GP film and sheeting, to highly sophisticated wear layers for premium-quality flooring, to high—temperature wire insulation, to car undercoatings, to the ultimate in highly plasticized products, namely, soft plastic fishing lures (typically 500–700 phr). The widely different requirements of these applications have resulted in the development of highly specialized plasticizers as well as GP types. The requirements of plasticizers for various illustrative applications are discussed in this section.

7.5.1 Overview

The versatility of PVC is, in large part, due to the wide range of useful additives including plasticizers. This can be seen in Table 7.12, where compounds range from hard and brittle (unplasticized, but included in the table for reference) to extremely soft and flexible. These compounds are generally formulated with GP plasticizers because there are usually no highly critical specifications that have to be met. On the other hand, the compounds shown in Table 7.13 involve specialty plasticizers because of the need to meet additional requirements—for example, better extraction resistance, lower volatility, better low-temperature flexibility, or easier processing.

7.5.2 Wire and Cable

Plasticized PVC remains the single largest volume electrical insulating material in use today. It has good electrical properties, has very good abrasion and moisture resistance, and may be formulated in a wide variety of whites, pastels, dark colors, and clears. Specified tensile strength properties are generally readily met with PVC. Flexible PVC insulation compounds are used in building wires, power cables, appliance wiring, automotive wiring, communications wiring, among others. PVC-insulated building wire is acceptable for use up to 600 V and 90 °C operating temperature of the conductor; appliance wires containing up to about 60 mil (1.5 mm) wall thickness meet performance requirements up to 15 kV direct current and 105 °C conductor temperature.

The Vinyl Institute has published results of an intensive investigation of the fire properties of PVC electrical insulation versus numerous other materials.[25] The report defines the critical characteristics of these materials with respect to fire

TABLE 7.12 Typical Properties of GP-Plasticized Vinyl[7]

	Rigid	Semirigid	Flexible	Very Flexible	Extremely Flexible
DINP plasticizer (phr)	0	34	50	80	600
Wt% of composition	0	25	33	44	86
			Typical Properties		
Specific gravity, 20/20 °C	1.40	1.26	1.22	1.17	1.02
Hardness, Durometer A, 15 s	—	94	84	66	<10
Flexural stiffness[a] at 23 °C:					
psi	$>130{,}000$	10,000	1700	500	—
kg/cm^2	>9140	703	120	35	—
Tensile strength:[b]					
psi	>6000	4500	3100	2000	—
kg/cm^2	>422	317	218	141	—
Elongation (%)	<15	225	295	400	—
Brittleness:[c]					
°C	>23	-16	-32	-47	—
°F	>73	$+3$	-26	-53	—
Examples (unfilled or low filler levels)	Bottles, pipe, siding, records	Shades, shoe heels, thin films, produce wrap	Wallcoverings, bookbinders, upholstery, garden hose	Boots, inflatables, gloves, water beds	Fishing lures

[a] ASTM D 747.
[b] ASTM D 882.
[c] ASTM D 746.

TABLE 7.13 Typical Properties of Specialty-Plasticized Vinyl Products[7]

	Automotive Upholstery	Waterstop	Building Wire	Refrigerator Gasket	Floor Tile
Composition[a] (phr):					
PVC	100	100	100	100	100
Plasticizer	67	67	60	90	33
Filler	9	19	28	74	533
		Properties			
Specific gravity	1.23	1.25	1.33	1.40	2.24
Hardness, Durometer A, 15 s	73	67	78	68	>95
Flexural stiffness (ASTM D 747) at 23 °C:					
psi	900	680	710	600	20,000
kg/cm^2	63	48	50	42	1410
Tensile strength (ASTM D 882):					
psi	2200	2000	2500	1800	900
kg/cm^2	155	141	176	127	63
Elongation (%)	360	350	300	275	8
Brittleness (ASTM D 746):					
°C	−37	−45	−29	−40	>23
°F	−35	−49	−20	−40	>73

[a] All compositions and properties are "typical"; plasticizer and filler types are varied to provide desired properties. Other ingredients (stabilizers, lubricants, colorants, etc.) are not shown.

initiation, propagation, and combustion products, concluding that while PVC is unique, it is not more hazardous than other electrical insulating materials.

In developing PVC insulation and/or jacketing compounds, plasticizer selection is a critical first step because of the profound effect plasticizers have on the key specification—retention of tensile properties after heat aging. Table 7.14 summarizes the preferred choice of plasticizers for various specified PVC wire insulations. The primary limiting criterion in plasticizer selection is the retention of elongation after a specified oven aging test condition. Many plasticizers are supplied containing phenolic antioxidants, to help improve plasticizer performance in accelerated aging testing. In some cases, low-temperature flexibility requirements dictate the use of elevated plasticizer concentrations or the use of linear phthalate plasticizers, augmented in certain applications with aliphatic dibasic acid esters.

Table 7.15 lists the preferred plasticizers for typical grades of PVC insulation specified by various industry and regulatory groups. The least stringent aging requirements are 7 days at 100 °C, which are the conditions required for 60 °C-rated PVC formulations; these requirements can be met with GP plasticizers such as DOP. Flexible PVC products rated for 75–80 °C performance require less volatile plasticizers such as DINP, DIDP, DPHP, or 711P types. Performance ratings for even higher temperatures (i.e., 90 and 105 °C) require the low volatility of

TABLE 7.14 Summary of Plasticizers[a] for Wire and Cable

Wall Thickness (mil)	Oven Test Temperatures Required for 7-Day Aging[b]			
	100 °C	113 °C	121 °C	136 °C
8	DIDP, DPHP	UDP, DUP	DUP, DTDP	TINTM, TOTM
15	DIDP, DPHP	UDP, 911P, DUP	DUP or DIDP/DTDP	50.50 UDP/TINTM, 25/75 DUP/TOTM
30	DINP, DIDP,[c] DPHP	DIDP	DIDP	75/25 DTDP/TINTM
60	DIDP,[c] DPHP,[c] DINP	DIDP, DPHP	DIDP, DPHP	DTDP, DUP

[a] All plasticizers contain appropriate antioxidant level.

[b] Some level (5–10%) secondary plasticizer or hydrocarbon extender can be added.

[c] Oven air flow of 100–200 air changes/h. Retained elongation requirements of >70%.

higher-molecular-weight phthalates and/or trimellitates. In all cases, the optimum plasticizer choice is a function of wall thickness and other factors influencing oven aging resistance, along with the other specified performance criteria.

To pass the 90 or 105 °C requirements, the PVC insulation is tested at 136 °C for 7 days. Common practice in the 1970s was to use the trimellitate TOTM as the sole plasticizer at about 50 phr. Efforts to reduce overall formulation costs proved that some of the trimellitate can be replace with lower-costing phthalate plasticizers such as DUP, L11P (DUP), or DTDP. Careful control of the manufacturing process allows the formulator to optimize costs by increasing the phthalate ester content while decreasing the trimellitate concentration. Using the higher-molecular-weight trimellitate TINTM instead of TOTM enables the use of even higher proportions of phthalate esters, all the while still meeting the appropriate performance standards such as those described in UL83.

The impact of phthalate blending and choice of plasticizer type on the retained elongation is shown in Fig. 7.4, recorded for the following typical 105 °C building wire insulation formulation:

PVC (suspension, K71)	100
Plasticizer	50
$CaCO_3$	15
SP-33 clay	15
Dibasic lead phthalate	6
Sb_2O_3	3
Stearic acid	0.3

In looking at blends of phthalates and trimellitates, as the ratio of the phthalate plasticizer is increased, a decrease in the retained elongation (after aging at 136 °C for 7 days) is realized. For DTDP/TOTM blends, the retained elongation falls

TABLE 7.15 Preferred Plasticizers[a] for PVC Electrical Insulation[7]

Aging Requirements[b]	PVC Insulation Specification	Preferred Plasticizer
7 days at 100 °C	60° Building T, TW, UF (UL 83 & 719)	DIOP, DOP, DINP, DIDP, 610P, DPHP, DOTP, 711P, L9P; blends with DINA and extenders
7 days at 100 °C	60° Class 11 (UL 62) Cord & Fixture	As above
7 days at 100 °C	60° Appliance (UL 758)	As above
10 days at 100 °C	75° Class 12 (UL 62) Cord & Fixture; NM-B Jacket (UL 83 & 719)	DINP, DOTP, DIDP, DPHP, 711P, L9P
7 days at 113 °C	80° Appliance (UL 758)	DINP, DOTP, DPHP, DIDP, 610P, 711P, L9P, DIDP/DINA blends
7 days at 113 °C	SAE-80[c], 24 mil	DINP, DIDP, 610P, 711P, L9P
7 days at 113 °C	SAE-80[c], 18 mil	UDP, DTDP, DUP, 911P
7 days at 113 °C	Semirigid (UL 1061) 8 mil wall	UDP, DTDP, DUP; blends with trimellitates
7 days at 121 °C	75° Building THW (UL 83 & 719)	DIDP,[d] UDP, blends DIDP with UDP, DTDP, DUP
7 days at 121 °C	75° Building, THWN, Nylon Jacket (UL 83 & 719), 15 mil PVC	UDP, DTDP, DUP; blends with DIDP
7 days at 121 °C	80° Appliance (CSA)	UDP, DTDP, DUP
7 days at 121 °C	90° Appliance (UL 758)	UDP, DTDP, DUP, blends[e] with DINA and/or trimellitates
7 days at 121 °C	90° Class 12 (UL 62) Flexible Cord & Fixture	UDP, DTDP, DUP, blends with DIDP
14 days at 121 °C	105° Appliance (CSA)	TIOTM, TOTM, TINTM; polyesters[f]
7 days at 136 °C	NM-B 90°, Building, Dry; THHN 90°, Dry, Nylon Jacket (UL 83 & 719)	TIOTM, TOTM, TINTM, blends with UDP, DTDP, DUP
7 days at 136 °C	105° Appliance (UL 758)	As above
7 days at 136 °C	105° Class 12 (UL 62) Flexible Cord & Fixture	As above
7 days at 136 °C	105° Flat Wire, computers (UL 62)	TIOTM, TOTM, TINTM, NODTM

[a] All plasticizers contain appropriate antioxidant.

[b] Forced-air oven; air exchange 100–200 times/h.

[c] SAE requires ASTM air exchange rate at 100–150 times/h.

[d] DIDP marginal pass; blends with higher-molecular-weight phthalates have improved aging resistance.

[e] DINA to enhance low-temperature performance; trimellitates (TM) blends for thin wall.

[f] Trimellitates for >1/64 in wall thickness; higher-molecular-weight polyesters for <1/64 in (15 mil; 0.4 mm) wall.

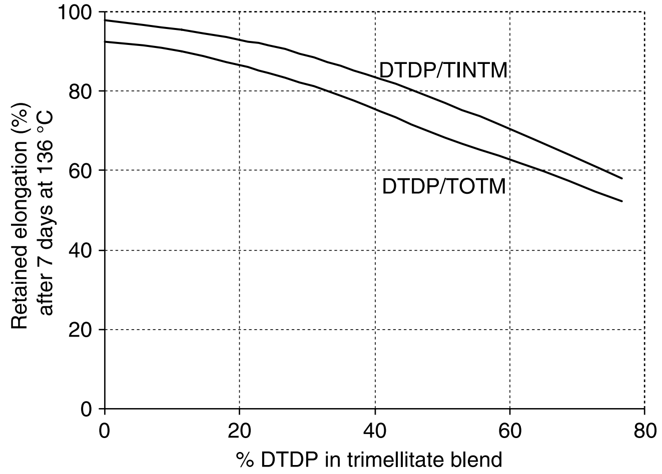

Figure 7.4 Retained elongation in 50 phr DTDP–trimellitate blends.[18]

below 70 percent when the DTDP level exceeds about 46 percent in the plasticizer blend. However, in blends with TINTM, the retained elongation will be over 70 percent until the phthalate level exceeds about 60 percent in the plasticizer blend. Thus, the formulator using TINTM as the starting point can achieve a greater cost savings versus that TOTM as a starting point, since higher levels of the lower-cost phthalate DTDP can be used.

Plasticizer type and concentration can impact insulating properties such as volume resistivity. Volume resistivity decreases with increasing plasticizer concentration. This effect is one of the reasons that many formulators add only enough plasticizer to pass the minimum tensile property requirements. (however, formulators will often increase the total plasticizer concentration to help improve retained tensile properties after aging). Plasticizer type also has an impact on resistivity. At constant plasticizer concentration, plasticizers exhibiting improved low-temperature performance will yield poorer resistivity measurements.[26] This suggests that a compound prepared with the partial replacement of trimellitate with DTDP would yield a higher resistivity than the corresponding compound prepared with a TOTM and DUP blend.

Calcium carbonate is the most common filler, but primary insulation compounds generally include calcined clay as a significant portion of the filler system to enhance electrical resistivity. Lead stabilizers have traditionally been used because of the outstanding stabilizing and electrical properties imparted, especially in the wet electrical aging tests. New mixed metal powdered nonlead stabilizers are becoming available for high-temperature insulation compounds, which pass the troublesome wet electrical testing requirement.[27] Lead replacement in wire and cable is discussed in Section 4.1.1 Clear flexible PVC insulation provides sufficient resistivity to be used in decorative low-voltage applications such as lamp cords and telephone hand sets. These formulations are free of fillers and require nonlead stabilizers.

Other ingredients common to wire jacketing and insulation compounds are discussed in separate chapters.

Table 7.16 shows typical performance properties of phthalate/trimellitate plasticizer blends in PVC formulations tested at both 15 and 30 mil (0.38 and 0.76 mm) thickness for 7 days at 136 °C.

Other properties influenced by plasticizers include low-temperature flexibility, extraction and migration resistance, flammability, and smoke resistance. Moy has shown that at 50 phr, a DIDP formulation containing 6 phr of antimony trioxide gives a PVC jacketing compound a limiting oxygen index (LOI) of 29.8. If a phosphate ester such as isopropylphenyl diphenyl phosphate is used to replace 50 percent of the DIDP in the same formulation, the LOI increases to 31.1.[28] Processing, especially dry blending, is also influenced by the plasticizer system. With the use

TABLE 7.16 Wire and Cable Insulation Performance[a]: Blends of High-Molecular-Weight Phthalates and Trimellitates[7]

Properties	UDP Blends			DTDP Blends	
Jayflex UDP	25	20	10		
Jayflex DTDP				20	10
Jayflex TINTM	25	30	40	30	40
PH/TM ratio	50/50	40/60	20/80	40/60	20/80
Original Properties (15 mil)					
Shore D hardness	45	45.4	46.2	46.3	45.9
Modulus at 100% elongation (psi)	2490	2500	2630	2570	2560
Tensile strength (psi)	3000	3000	3330	3350	3060
Elongation (%)	225	265	255	269	221
Aged 7 Days/136 °C (15 mil)					
Tensile retained (%)	135	109	102	96	111
Elongation retained (%)	44	58	81	53	96
Weight loss (%)	10.1	8	4.5	6.2	3.6
Original Properties (30 mil)					
Modulus at 100% elongation (psi)	2450	2490	2510	2550	2520
Tensile strength (psi)	3030	2790	3120	3160	3100
Elongation (%)	286	224	306	267	270
Aged 7 Days/136 °C (30 mil)					
Tensile retained (%)	100	104	97	94	97
Elongation retained (%)	63	67	85	85	87
Weight loss (%)	6.7	5.5	3.0	3.8	2.4

[a] Formulation: PVC, 100; plasticizer, as shown, antimony trioxide, 4; Dythal® stabilizer, 6; SP-33 clay, 12; stearic acid, 0.2.

of trimellitate and phthalate blends such as TINTM with DTDP, problems may arise in being able to obtain a quality dry blend. Preheating the plasticizer to about 70 °C before the plasticizer is added to the dry blending mixer usually eliminates this problem. The use of phosphate plasticizers is discussed in Chapter 9.

7.5.3 Film and Sheeting

Flexible PVC film and sheeting products are typically made by the calendering process. Supported (e.g., fabric-backed or mesh-reinforced) products are made by laminating, calender coating, or plastisol casting processes. Small-volume specialty film and sheeting products are sometimes made by the extrusion process. The terminology "film" versus "sheeting" reflects thickness; Less than 8 mil (0.2 mm) gauge is termed "film," whereas "sheeting" thickness is 8 mil or more. Typical end-use products made with flexible PVC film and sheeting are as follows:

Indoor	Outdoor
Bookbinders, stationary	Awnings
Laminating films	Back-lit signs
Luggage	Boat covers
Travel cases	Marine upholstery
Sporting equipment	Patio furniture
Packaging	Truck tarpaulins
Shower curtains	Geomembranes
Tablecloths	Pool liners
Upholstery	Inflatable shelters
Wallcoverings	Rainwear
Waterbeds	Roofing membranes

These products are formulated for optimum cost/performance characteristics for the specific use. The majority of these applications can utilize GP plasticizers such as DINP, DOP, or DOTP. Linear or straight-chain phthalates such as 711P-, L9P-, or 610P-type plasticizers, are used for improved low-temperature properties and improved oxidation resistance, while DIDP is used for lower volatility and improved diffusion resistance. For improved resistance to migration into nitrocellulose furniture finish, one may choose DOTP or a DIDP/hydrocarbon secondary plasticizer blend. Adipate esters can be used in combination with GP plasticizers to improve low-temperature performance. Plasticizer choices other than these are made only as necessary to provide required performance characteristics.

Stationary end uses include three-ring notebook binders, as well as various vinyl covers for checkbooks, pocket calendars, and so on. Performance requirements are defined for four different grades of vinyl bookbinders in a commercial standard.[29] Class 90 bookbinder has the lowest cost composition, having no critical performance parameters defined. Class 100 requires that the bookbinder film demonstrate 80 percent pass in the Masland Impact Test (ASTM D 1790) at 0 °F (−18 °C), as well as limited volatility in the activated carbon test (ASTM D 1203). It is typically formulated with 40 phr 711P as the primary plasticizer; a product of similar properties is provided by the use of 43 phr of an 80/20 weight percent blend of DINP/DINA. Class 110 bookbinder must meet the Masland requirement at −10 °F (−23 °C); it is typically formulated with 40 phr of a 75/25 weight percent blend of 711P, 610P, or 810P plasticizers in order to meet the low-temperature properties. Class 120 is a specialty product, typically formulated with 30 phr of a linear adipate ester in order to pass the Masland Impact Test at −20 °F (−29 °C).

Bookbinder formulas typically contain about 10 phr of calcium carbonate filler, but the filler level may be adjusted between zero and about 20 phr in order to optimize cost/performance of specific bookbinder products, depending upon gauge, color, embossing and desired "hand." The more costly grades, 100–120, typically employ an additional 5 phr of an acrylic processing aid, which enhances hot strength at the calender stripping roll. (The acrylic process aid can often improve durability of an embossed surface). Bookbinder products sometimes encounter classic problems related to plasticizer diffusibility—rejection of printing inks, transfer of copying inks to the binders, and "crinkling" (distortions or loss of dimensional stability). Printability is controlled by limiting the use of plasticizers and other formulating ingredients having limited compatibility in PVC. The "crinkling" failures are often the result of plasticizer migration, which occurs when notebook fabrication brings PVC films together which have different plasticizer concentrations or different diffusibility characteristics. Poppe[30] showed that "crinkling" notebook failures differentiated low-molecular-weight and more linear plasticizers from the less diffusible DIDP, which is preferred due to its higher molecular weight and degree of branching.

Wallcovering employs about 65 phr GP phthalate plasticizers; heavy gauges use higher plasticizer levels, while thinner gauges use 50–55 phr. Wallcovering may employ about 5 phr antimony trioxide as a flame retardant; unfilled systems may use 5–10 phr of chlorinated paraffin to help improve the flame retardancy. The following is a typical formulation for wall coverings, prepared by spread coating of fabric:

PVC (dispersion resin)	100
DINP	65
ESO	3
$CaCO_3$	5
Sb_2O_3	4
Ba/Zn stabilizer	3
Pigment	as required

PVC roofing membranes and inflatable shelters impose the most critical requirements for flexible PVC weathering resistance, where product life of greater than 20 years is often expected. Direct exposure to outdoor weathering conditions involves a multitude of degradative forces, requiring a complex package of formulating additives.[31] The optimum plasticizer selection is influenced by the most critical exposure elements. As a rule, linear phthalates show improved ultraviolet and oxidative stability over branched phthalates, but even branched phthalates such as DIDP or DPHP perform acceptably well in membranes properly formulated with a variety of additives, including UV absorbers, hindered amine light stabilizers, and other additives. Trimellitates, however, are less resistant to outdoor weathering than their phthalate counterparts, and aliphatic dicarboxylic acid esters are deficient in long-term compatibility. Linear, low-volatile phthalates such as L911P, DUP, and L11P are generally preferred, but lower-cost 711P types have also demonstrated long product service life. For example, it is known that white, reinforced flexible PVC sheeting containing 711P has provided acceptable service for greater than 15 years in the north temperate zone. Branched phthalates, such as DIDP, have been found to be preferred over some linear phthalates under ballasted roofing applications, where plasticizer diffusibility is a critical limitation.[32] These same authors have reported that installed roofing membranes of flexible PVC have been analyzed and tested periodically for up to 8.5 years. Slight loss of plasticizer is observed during the initial time period of exposure, but this is followed by a chemical change in the surface of the exposed PVC, which reduces further loss of plasticizer.

Alloys of PVC prepared with high-molecular-weight ethylene–carbon monoxide (CO)–ester terpolymers are finding increasing use in PVC roofing membranes. To help offset some of the formulation costs, lower-cost branched phthalates such as DIDP or DPHP are being used as partial replacement of the linear phthalates and the ethylene–CO–ester-type polymeric plasticizers.

The following is a starting roofing formulation:

PVC (high molecular-weight homopolymer)	100
L9P	30
Ethylene–CO–ester terpolymer	30
ESO	3
TiO_2 (rutile, surface-coated)	10–15
UV absorbers	0.5–1
Mixed metal stabilizer	3
HALS	0–1
Antioxidant	0.5
Biocide	1–2
Lubricant	0.3

Geomembranes represent another commanding application for plasticized PVC products. These can be used as landfill liners, as canal liners, in mining applications, and in pond and pit liners in various types of construction. Flexible PVC geomembranes offer advantages over other polymer systems in their better resistance to settlement, puncture resistance, and seam control. Plasticizer choices for geomembranes are dependent upon the specific application requirements. Linear plasticizers such as 711P or 911P will offer better low temperature performance, while branched plasticizers perform better in extremely acidic or caustic environments and in terms of their lower migration rates into caustic liquids or solids.[33] General guidance is to use plasticizers that have a molecular weight above 400 to ensure greater retention such as DINP, DIDP, DPHP, and L9P. The new specification PGI-1104 issued by the PVC Geomembrane Institute reflects this requirement. This same specification precludes the use of adipates and chlorinated secondary plasticizers. The following is a starting-point formulation for a PVC geomembrane:

PVC (K71)	100
DIDP	55
$CaCO_3$	5
TiO_2 (rutile, coated)	5–10 as required
Carbon black	2–4
Ba/Zn stabilizer	2.5
Ester lubricant	0.5–2
UV stabilizers	0–2 as required
Pigments	as required
Biocides	1–2
Antioxidant	0.5

Flexible PVC films are also used in agriculture applications (e.g., seedling protection, weed control, and green house coverings), primarily because they last longer than their polyolefin equivalents. For agriculture film, a good starting formulation is the following:

PVC	100
DIDP	50
Triaryl phosphate	5
Epon 828	3
Ba/Zn stabilizer	2
Antifogging agent	2–4
Stearic acid	0.25

Tarpaulins can be made through both calendering and spread-coating techniques, where the PVC top coat is bonded to a polypropylene or polyester support. GP plasticizers are most commonly used; linear plasticizers or even DIDP can be used for improved outdoor aging resistance. Often, for transportation requirements, some level of flammability protection is required. The following is a starting low-flammability top coat formulation for use is spread coating production:

PVC (dispersion)	100
DIDP	50

Diisodecyl phenyl phosphate	25
Antioxidant	0.7
UV absorber	1
Sb_2O_3	3
TiO_2 (rutile, coated)	3
Ba/Zn stabilizer	3

7.5.4 Flooring

PVC is used in a variety of flooring products, including floor tile, sheet flooring, carpet tile backing, walk-off mats and wall base (formerly called "cove base"). Each of these has distinct requirements—both in processing and in end use.

7.5.4.1 Floor Tile Various types of vinyl floor tile are made in the United States at present, including vinyl composition tile for both commercial and residential markets and homogeneous tile (also called "solid vinyl tile").

Vinyl Composition Tile This type of tile represents the current derivative of the original vinyl asbestos tile (VAT). Asbestos was used in the past to impart hot strength during processing and dimensional stability while in use. However, because of health concerns, it became necessary to reformulate and remove the asbestos. This was accomplished in part by converting to a slightly higher-molecular-weight and lower-acetate-content vinyl chloride/vinyl acetate copolymer (10 percent vs. 14 percent acetate). More recent advances incorporate low-molecular-weight homopolymer PVC as partial or complete replacement for the copolymer resins. Binder levels (PVC copolymer plus plasticizers) in the new composition tiles range from as low as about 15 percent to as high of about 22 weight percent.

Furthermore, the increased ability to process at higher temperatures reduced the need for strong-solvating plasticizers in the new composition tiles. Thus, GP plasticizers, such as DOP and DINP, are currently used at 50–100 percent of the plasticizer system. When they are not used as the sole plasticizer, the balance is a stronger-solvating plasticizer, such as BBP, DIHP, or a benzoate ester, which improves processability.

Homogeneous Tile This type of tile has a binder level of about 40 weight percent. Aside from use in flooring, novel and more decorative tiles can also be used as wall and countertop coverings. The higher binder level of homogenous vinyl tile imparts more styling latitude and strength properties required for the nonflooring installations. GP plasticizers are used to reduce fuming at the higher processing temperatures, as well as to lower cost and specific gravity. However, as with composition tile, some commercial-grade homogenous tiles continue to employ strong-solvating plasticizers such as BBP or DIHP, sometimes up to 50 percent of the plasticizer system.

7.5.4.2 Sheet Flooring These products are made by calendaring/laminating and plastisol spread coating. The calendered products cover a range from low to fairly high cost, while the products made by spread coating range from moderate to expensive, the latter being very sophisticated multilayer constructions. Most calendered products use PVC homopolymer and GP plasticizers, such as DOP and DINP.

The more sophisticated products, based on plastisol technology, are quite complex in construction. The requirements for each layer differ significantly, as do their formulations. Thus, clarity and stain resistance are of key importance in the wear layer, whereas foam quality is another major concern in the foam layer. In some sheet flooring products, the backing material is bottom-coated with a PVC layer.

Formulations for the very sophisticated multilayer products are closely guarded proprietary information, but it is known that it is necessary to use special dispersion resins to achieve the highest clarity in the wear layer; in fact, it is common to use two or more resins to achieve an optimum balance of rheological properties and clarity. Many of the vinyl formulations currently used in sheet flooring have been optimized around the use of more cost-effective plasticizers such as DIHP and BBP, which in addition have desirable solvating characteristics. Other plasticizers used in sheet flooring include viscosity-depressant types such as Jayflex® 215 and TXIB.

7.5.4.3 Carpet Tiles and Walk-Off Mats These widely used products often use vinyl plastisols for face fiber tuft lock and backing. The backing enhances dimensional stability and provides slip resistance. When foamed, they contribute to comfort. The critical performance requirements for plastisols for these applications include the following:

- The precoat must have appropriate viscosity to allow controlled penetration of the porous web to provide bonding with the tufts.
- The backing layer must readily bond to the precoat under cure conditions that will not damage the tufts.
- The foamed backing must form a closed cell foam.
- Dimensional stability and strength must be imparted, particularly along the edges.

These properties are all influenced by the vinyl resin, plasticizer type and concentration, as well as by rheology-control agents (viscosity depressants and thickness). The face fibre are often heat-sensitive (e.g., polypropylene fibers). Therefore the PVC polymers are typically low-molecular-weight vinyl chloride/vinyl acetate copolymers. Plasticizer levels range from 60 to 100 phr. The common practice is to use faster-fusing phthalate DIHP as the sole plasticizer or to use DIHP in dilutions of up to 50 percent with a GP-type plasticizer such as DINP.

For vinyl carpet backing, the following is a starting formulation:

PVC	75
PVC copolymer (10 percent vinyl acetate)	25
DIHP	100
$CaCO_3$	250
Ca/Zn stabilizer	2
Carbon black	1.5
Drying agent (CaO)	5

Table 7.17 shows starting place formulations for chair mats and flexible runners, both of which may be grouped with vinyl flooring products. These products are made by the extrusion process. The semirigid chair mat at 25 phr plasticizer is typically compression-molded into the final shape, following extrusion. The flexible runner

TABLE 7.17 Starting Place Formulations: Vinyl Chair Mats and Runners[7]

	Clear Chair Mat	Conductive Chair Mat	Flexible Runner
PVC, suspension grade	100	—	100
VCl/VAc copolymer, dispersion grade	—	100	—
79P	25	—	—
DOP	—	—	55
DIDP	—	76	—
ESO	5	5	5
Stabilizer	2	3	2
Lubricant	0.3	—	0.3
Conductive pigment	—	4	—
Fungicide	—	1	—
Typical Properties			
Specific gravity at 20/20 °C	1.28	1.17	1.21
Hardness:			
Durometer A	—	67	76
Durometer D	50	—	—
Modulus at 100% elongation:			
psi	2950	880	1330
kg/cm^2	208	62	94
Tensile strength:			
psi	3370	2120	2670
kg/cm^2	265	149	188
Ultimate elongation (%)	275	365	350
Clash–Berg[a] T_f (°C)	2	-45	-33
Brittleness[b] T_b (°C)	-14	-47	-38

[a] ASTM D 1043.

[b] ASTM D 746.

is extended into a pair of embossing rolls that impart different patterns for the top and bottom of the runner.

7.5.4.4 Wall Base

Extruded vinyl wall base is opaque and generally in black or dark colors. some product is produced through coextrusion techniques. Here, the top coat can be very colorful, while the base material contains a lot of recycled material. It is important that the level of recycled material be controlled because of its impact on extrudability (gauge variations and dimensional stability problems). Exceptionally high levels of lubricant are often used to improve processability.

Other than dimensional stability, the next most critical performance requirement of wall base is retention of adhesion. A primary concern is the potential for plasticizer migration into the adhesive. Acceptable performance is accomplished by careful selection of the type of adhesive and by limiting the phr level of the plasticizer in the wall base. GP plasticizers (DINP or DOP) are often used in combination with a strong solvator (BBP or DIHP) to achieve a balance of processability, resistance to plasticizer migration into the adhesive, and cost. Appropriate selection of adhesive is critical to the successful use of cost-effective GP plasticizers.

7.5.5 Plastisols

The selection of plasticizer type and concentration for plastisols is strongly influenced by process limitations—plastisol viscosity, viscosity stability, and gelation, and fusion characteristics in addition to cost and end-use performance requirements. Plastisol processes are distinct, in that the plastisols are shaped into the desired form while still in the paste stage, and then exposed to heat for gelation and fusion into finished products. "Hot compounding," in contrast, involves shaping of the hot plastic in the fluxed state. In some plastisol processes, the shaping occurs simultaneously with the early part of the gelation cycle, as with vinyl foams, carpet back adhesives, rotomolding, and cast traffic cones, for example. An attractive feature of the plastisol process is that products formed in this manner are free of residual stresses, which would impair dimensional stability in durable applications—an undesirable feature is that plastisol resins are typically more costly than suspension resins.

Extensive varieties of plastisol processes have been described in the literature. In addition to careful selection of plasticizer type and concentration, the formulator may select from a wide variety of other additives to control critical plastisol properties. Formulation optimization must then be carried out under conditions simulating the manufacturing process. This includes rheological properties as a function of various shear rates and as a function of plastisol age, as well as thermal effects on gelation and fusion under process conditions. For example, viscosity stability is critical for a plastisol that may be stored in a hot warehouse that may reach a temperature over 100 °F (38 °C). Increased plastisol viscosity results from plasticizers penetrating and swelling the PVC resin particles—an irreversible process once initiated. Slush, dip, and rotomolding processes involve low shear rates in the forming cycle; Brookfield viscosity measurements are typically applied to control and monitor plastisols used in these processes. Plastisols for high-shear-rate processes, such as spray, knife, and reverse roll coatings, must be evaluated with instruments such as the Burrell–Severs capillary rheometer. Furthermore, it is frequently necessary to control plastisol rheology over a range of shear rates. An extreme case is automotive underbody coating (UBC), whereupon no "sag" is allowable under essentially zero shear rate immediately following the high-shear spray application of the plastisol to the auto underbody. For these processes, it is often helpful to use viscosity-modifying additives in the plastisol.

Wadey et al.[8] compared the effects of chain branching on plastisol viscosity in a series of differing diisononyl phthalates. Slightly branched DINP gave a plastisol viscosity about 17 percent lower than did commercial-grade moderately branched DINP. The 2-methyl branched and normal nonyl phthalates gave plastisol viscosities 44 percent and 58 percent lower, respectively. Highly branched DINP plasticizers contained tertiary carbons in the alkyl backbone; these plasticizers gave plastisol viscosity about 12 percent higher than did the moderately branched DINP.

Table 7.18 provides a summary comparison of plasticizers commonly used in plastisols and allows for some generalizations as a function of plasticizer structure; all compositions tested were unfilled plastisols containing 70 phr plasticizer. These generalized observations at equal phr are as follows:

- Overall, 610P gave similar performance to 711P. The primary difference is that initial viscosity under both low and high shear rates is about 25–30 percent lower for the 610P plastisols than for the 711P plastisols. The branched alkyl phthalates showed significantly higher initial viscosity than did the linear phthalates; DINP and DIDP are about 50–60 percent higher than the 610P and 711P

TABLE 7.18 Comparison of Plasticizers in Plastisols[a],[7]

Plasticizer	610P	711P	DINP	DIDP	DIDP/DINA 85/15
SPI air release, Huff ring (s)	37	41	28	22	18
Hot bench gelation temperature:					
°C	107	106	109	118	119
°F	225	222	228	244	246
Brookfield viscosity, 2 hours at 25 °C (cP):					
3 rpm	1660	2440	3200	3480	2670
30 rpm	1480	1980	2620	3030	2110
Viscosity after aging 7 days at 38 °C:					
3 rpm	5450	8000	6270	6440	5150
30 rpm	3330	4590	4060	4360	3190
Severs viscosity, 2 hours at 25 °C (P):					
Shear rate (s^{-1}):					
100	20	25	48	63	60
500	32	43	73	101	96
1000	34	44	72	100	91
1500	35	45	76	103	98

[a] Formulation: PVC (Geon® 121), 100; plasticizers (as shown), 70; Mark® 7101, 2.5.

plastisols, respectively, under low-shear-rate conditions and about 2–2.7 times higher, respectively, at high shear rate. Note, however, that after aging 7 days at 38 °C (100 °F) the viscosities of the straight-chain and linear phthalate plastisols are much closer to those of the branched phthalate plastisols.

- The stability of plastisol viscosities was measured at low shear rate after aging up to 7 days at 38 °C (100 °F). Viscosities of the 610P and 711P plastisols increased by about 2–3 times, whereas the viscosities of the branched plasticizer plastisols increased by about 1.5–2 times: the 15 percent DINA in DIDP had no significant effect on viscosity stability.
- Air release is significantly improved with increased plasticizer branchiness and molecular weight. DINP and DIDP were significantly faster in air release than were 610P and 711P, but blend of 15 percent DINA and DIDP showed the most desirable air release properties of all; it was twice as fast as the 610P and 711P and controls. In fact, the original work in this study[7] included plastisols made with 70 phr of the adipates: DINA, DOA, and the linear 79A. It showed that air release properties of phthalate/adipate blends are directly related to the ratio of adipate used, and that moderately branched DINA is the most effective plasticizer to enhance air release. These observations are consistent with reports by other investigators.[34,35]
- Hot bench gelation temperature is lowest for 610P and 711P. Compared with these phthalates, DINP required about +3 °C, and DIDP about +12 °C. The 15 percent DINA in DIDP blend had only a marginal effect of +1 °C versus DIDP on hot bench gelation, while the 100 percent DINA sample yielded about +12 °C over the DIDP sample in gelation temperature.

While hot bench gelation differentiates the effect of branchiness in phthalate plasticizers.[36] Figure 7.5 shows that gelation measurements by dynamic mechanical

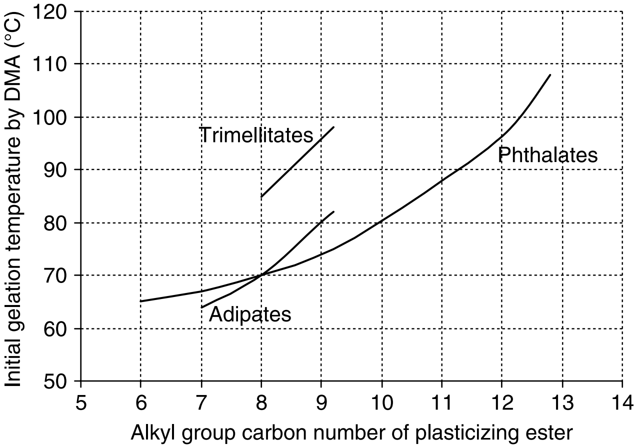

Figure 7.5 Initial gelation temperatures versus carbon number.[36] Formulation: PVC, 100; plasticizer, 70; liquid Ba/Cd/Zn stabilizer, 2.0.

analysis (DMA) do not differentiate straight-chain and linear versus branched phthalates, even though that procedure does show a distinction of the various chemical families of plasticizers and the effect of varying alkyl carbon numbers.

7.5.6 Dry Blending

Plasticizer type and concentration have significant effects on the dry blending process and quality of the dry blend, as do the physical characteristics of the PVC resin. DIDP is a plasticizer widely used in commercial dry blending processes. Plasticizers whose molecular weight and degree of branching are lower than those of DIDP dry blend readily. Plasticizers of higher molecular weight or of having a higher level of branching are more difficult to process into a dry blend of acceptable quality. ASTM D 2396 is the test method generally used to compare the dry blendability of PVC formulations. This method allows for comparing plasticizers by using a single resin (in this case, Georgia Pacific GP-2095) and the specified formula. Figure 7.6 is a result of data generated in this fashion. It shows that the dry-blending process is distinctly influenced by plasticizer type—for example, phthalates versus trimellitates versus adipates—as well as by the level of branching and plasticizer molecular weight.

In the dry blending process, the plasticizer penetrates the interior of the PVC resin particle, solvating the amorphous but not the crystalline regions of the polymer. Naturally, plasticizer solvency and plasticizer viscosity affect the dry blending rates. Krauskopf and Godwin[37] examined the correlation of dry blend times for 18 commerical plasticizers with several plasticizer properties, including plasticizer viscosity, specific gravity, and plastisol gelation and fusion temperatures. Figure 7.7 graphically compares their measured blend times as a function of the viscosity of each plasticizer determined at 88 °C. The data shows that viscosity is one of

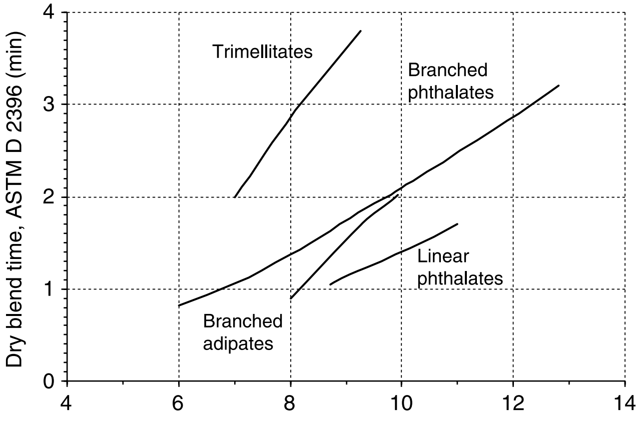

Figure 7.6 Dry blend time versus alkyl group carbon number.[37]

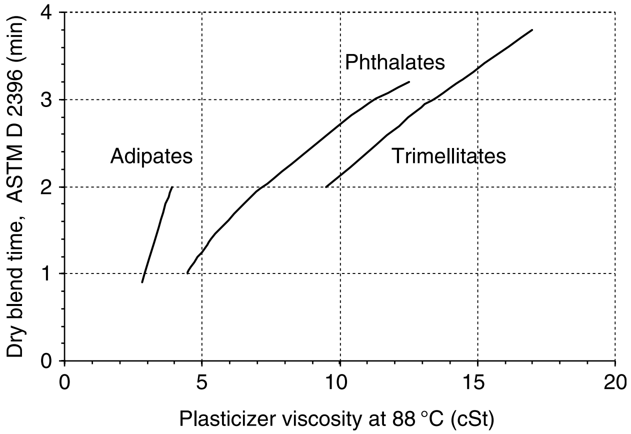

Figure 7.7 Dry blend time versus plasticizer viscosity.[37]

the primary independent variables controlling dry blend time, but it also shows that the chemical nature of the plasticizer likewise imparts a measurable influence. For example, at the same plasticizer viscosity, a phthalate ester will dry-blend faster than an adipate, and a trimellitate ester will dry-blend faster than a phthalate. The same study also found that the specific gravity of the plasticizer has a small degree of correlation with dry blending times, as higher-specific-gravity plasticizers will dry blend faster than lower-specific-gravity materials. Dry blending is also discussed in Chapter 13.

7.5.7 Automotive

Plasticized PVC is still widely used in the automotive market although the volumes continue to decline. These application areas for flexible PVC include the following:

Seat upholstery
Instrument panels
Molded arm rests and head supports
Gear shift dust covers
Seat splines
Sound-deadening panels
Window seals
Truck tarpaulins
Sealants of various types
Door panels
Steering wheel and horn button covers
Console and glove compartments
Trim laminating films
Floor mats
Wire insulation
Sidebody molding
Underbody coating
Grommets, gaskets, and electrical tape

In the early 1960s, automotive producers investigated a problem characterized as “windshield fogging,” the accumulation of tiny hydrophobic droplets on the interior of windshields. This caused impairment of visibility, especially in darkness and rain.

Basically, the oily fog is an accumulation of organic components that volatize in automotive interiors when closed up in the heat of the day, followed by condensation on cooled glass surfaces at night. The technical problem was ultimately characterized as "light scattering film" (LSF). Early analyses showed the presence of DOP plasticizer along with numerous other organic compounds. Because DOP- and DOP/DOA-plasticized PVC were widely used in automotive interior products at that time, automotive companies developed LSF performance requirements that precluded the use of DOP and other volatile components. Straight-chain and linear phthalates such as 610P and 711P initially became preferred plasticizers due to their lower volatility, good low-temperature properties, and favorable costs. However, the LSF problem was not completely resolved, partly because these relatively low-molecular-weight plasticizers passed the specified performance requirements by only a narrow margin. In the 1980s, the Ford Motor Company adopted a new LSF test using the Haake instrument, Type 001-1199. This method has tentatively been subscribed to by the Society of Automotive Engineers (SAE), leading to the development of the method SAE J1756. This standard has contributed to a more consistent method to characterize LSF performance characteristics of PVC parts and other automotive interior parts.

Duncan[38] established the capability of the LSF test using the Haake instrument. She demonstrated not only that DOP consistently fails to meet the LSF requirements as defined by Ford, but its use contributes to wide variations in LSF values; this is probably due to co-distillation of low-molecular-weight nonplasticizer additives in the flexible PVC parts. Table 7.19 summarizes the current LSF requirements and the impact of plasticizer type versus the required test conditions.

The replacement of the more volatile plasticizers with low-fogging plasticizers such as DIDP, DPHP, L9P, 911P, DUP, and trimellitate esters has greatly reduced the fogging problem, to the extent that analyses of the residue collected from the interior windows rarely detect the presence of phthalates. Indeed, Howick[39] reports

TABLE 7.19 Plasticizers for Low-Fog Automotive Applications versus Test Requirements[a], [7]

	6 h at 85 °C	6 h at 90 °C	6 h at 95 °C	3 h at 100 °C	6 h at 110 °C
DINP	XX	X	X	X	F
711P	XX	X	X	X	F
DIDP, DPHP	XXX	XX	XX	XX	F
L9P	XXX	XX	XX	XX	F
911P	XXXX	XXX	XXX	XXX	X
DUP, L11P	XXXX	XXXX	XXXX	XXXX	XX
TOTM, TINTM	XXXX	XXXX	XXXX	XXXX	XXX

[a] Minimum of 70% retained reflectance, reported for neat plasticizer liquids in the Haake Fog Test Instrument. F = failure; X=marginal pass with <75% fog rating; XX=passes with values >75% and <90%; XXX=passes with values >90% and <95%; XXX=passes with values >95%.

that PVC articles have negligible contribution to automotive fogging and attributes many of the chemicals detected in his study, especially the amines, to chemicals used in various polyurethane materials.

Seat Upholstery Seat upholstery must meet specified “hand” characteristics, Masland low-temperature impact resistance, DOT (Department of Transportation) flame spread, and other specific requirements such as color stability under exposure to UV light. Rolls of prefabricated vinyl-coated substrate are typically made by plastisol spread coating and by calendering or laminating techniques. All vinyl upholstery products are supported with textile backing to give dimensional stability, and they may contain a clear topcoat of vinyl/acrylic to enhance stain resistance, plasticizer permanence, and product durability. These features, as well as plasticizer phr, can influence performance properties also affected by plasticizer selection. For more than two decades, 610P and 711P have been the preferred primary plasticizers, but these have now been replaced with the lower-cost branched plasticizers DIDP and DPHP. In some applications with a low-temperature requirement, L9P and L911P are used.

DOT MVSS No. 302 (Motor Vehicle Safety Standard) was developed in the 1970s in response to demands for flammability resistance of automotive interiors. The key performance requirement of MVSS 302 is that the upholstery material may not burn at a rate faster than 4 in/min (10.16 cm/min) when as 4 in × 14 in (10.16 cm × 35.56 cm) specimen is held horizontally by a specified apparatus and ignited by an open flame.

The upholstery starting place PVC formulation shown below has been found to meet MVSS 302, as well as the other performance requirements typically specified by automotive manufacturers (low windshield fogging, low-temperature flexibility, durability, etc.):

PVC	100
DIDP	65
Triaryl phosphate	14
ESO	5
Sb_2O_3	3
Stabilizer/lubricant (low-fog)	2.5

Critical variables other than plasticizer type include:

- Thickness of PVC coating
- Total plasticizer level (phr)
- Sb_2O_3 particle size
- Flammability resistance of cloth backing
- Effects of topcoat

High-quality, longer-life automobile upholstery must pass a rigorous oven aging test—500 hours at 121 °C (250 °F)—and must also have good flexibility at low temperature. These requirements may be met by heavier gauge and the use of more costly, higher-molecular-weight linear phthalate plasticizers, such as 911P and DUP.

Door Panel Covering Door panel covering is similar in appearance and composition to seat upholstery. However, for styling and assembly purposes, PVC door paneling typically consists of a vinyl foam layer sandwiched between flexible PVC films and laminated to a thermoformable backing or a vinyl sheet laminated to a polypropylene foam backing. The plasticizers of choice are typical of those shown for upholstery, predominately L9P, DIDP, and DPHP. The following is a possible starting point for a door panel covering:

PVC (suspension, K71)	100
DIDP	52
$CaCO_3$	5
Sb_2O_3	3
Ba/Zn stabilizer	3
UV additives	0.5–2
Lubricant	0.3

Instrument Panels Automotive instrument panels (IP) are manufactured by several different techniques. Thermoformed calendered sheet is the traditional process used to produce low-cost IPs. Slush-molded plastisols provide PVC IPs of more elegant styling (grain appearance and contour lines) with improved durability under the very rigorous exposure environment directly beneath automotive windshields. The plastisol molding technique, however, has generally been displaced by direct molding of PVC dry blends or powder blends, which impart improvements in styling register and thickness consistency at reduced costs. Powder blends are often prepared by cryogenic grinding of dry blends.

A typically starting place formulation would require 60 phr 911P. This plasticizer can meet the volatility and other performance requirements for some IPs. However, high-molecular-weight linear phthalates (e.g., L11P or DUP) and trimellitates—or blends thereof—are commonly used to optimize processability, volatility, and low-temperature properties, but at a significant price premium. Specialized low-volatility, low-fogging stabilizers are also necessary; some of these may require a perchlorate component to protect against discoloration from polyurethane chemicals.[40]

Thermoformed calendered sheeting requires the use of polymer alloys in order to maintain the embossed surface grain under the thermoforming process used for IP fabrication. These products are typically about 75/25 blends of flexible PVC/ABS (acrylonitrile–butadiene–styrene terpolymer). The plasticizer systems are similar to those used in the slush-molding process, except for occasional use of DIDP and other low-volatility phthalates as a partial component in the plasticizer blend for the primary purpose of cost reduction.

Sidebody Molding Extruded plasticized PVC provides a cost-effective automotive trim product having high durability and styling, while resisting impact dents caused by opening doors of adjacent vehicles. Color retention is primarily a function of pigment and stabilizer systems. Plasticizer choice is generally a function of the degree of softness (plasticizer phr) desired. Plasticizer use levels typically range from 50 to 70 phr; thin-gauge sidebody molding typically uses the lower plasticizer levels, while high plasticizer phr values are required for large-size molding. These products may use up to 25 phr calcium carbonate filler for cost optimization. The lower-phr formulas require a linear phthalate in order to meet low-temperature performance requirements, whereas branched phthalates such as DINP and DIDP are used in the softer formulations.

Underbody Coating (UBC) Asphaltic and Gilsonite coatings are not capable of meeting the current requirements of corrosion and stone-chipping resistance provided by plastisols. While many varied polymer systems have been evaluated for UBC, PVC plastisol technology provides optimum cost, performance, and applications versatility. Thus, several complex plastisol formulations are used to meet the requirements for application as UBCs, adhesives, and sealants. In some cases, paint compatibility is required where the finish comes in contact with the plastisol. This could occur in painting operations after the plastisol has been applied and then fused, or in other types of painting systems where the paint is applied over the wet, uncured plastisol.

Plastisol usage for automotive sealants is typically 10–20 pounds (4.5–9 kg) per vehicle. The plasticizer levels may vary over a range from 50 to 200 phr; likewise, the filler types and concentration vary widely, ranging from 30 to 600 phr. A typical formulation may start with 100 parts PVC copolymer, 100 phr DINP, 100 phr $CaCO_3$, plus adhesion promoters, viscosity control agents.

Critical performance requirements that influence plasticizer choice for sealant may include:

- Cost
- Compatibility with the application environment
- Low plastisol viscosity
- High plastisol yield value (anti-sagging)
- Low volatility
- Stability under high temperature
- Flexibility under low temperature (end use)
- Resistance to migration and staining
- High tolerance for filler loading

Linear phthalates, such as 711P, have been used in the past as they provided a good balance of overall properties at a reasonable cost. However, DINP is a cost-effective substitute. DOP and lower-molecular-weight phthalates may not meet all volatility requirements, while DIDP, DPHP, and higher-molecular-weight phthalates may fail some gelation or fusion requirements. Often, a lower-molecular-weight phthalate such as DIHP is used in blends with DINP to improve the gelation/fusion profile.

Plasticizers such as Texanol benzyl phthalate may be required to impart higher surface tension to the plastisol, which enhances paint compatibility. But even the use of this more costly plasticizer provides only borderline paint compatibility.

Traffic Cones Brightly colored flexible PVC replaced painted rubber highway traffic cones during the early 1970s when the cost of medium-thermal black rubber increased by a factor of five within one calendar year. The vinyl cones are composed of three distinct formulations which are fused together in the final stage of fabrication. The traditional process requires a series of casting and gelation steps, which are concluded by exposing the entire molded assembly in high-temperature fusion ovens. The fused, three-layer cone is then stripped from the mold and water-cooled.

The highly filled base formulation is designed to provide upright stability to the cones when exposed to high winds and physical forces along highways. The base formulation utilizes up to 300 phr of a calcium carbonate or barite filler. The plasticizer level is typically quite high, about 80–110 phr. The preferred plasticizer systems are typically GP-type plasticizers blended with stronger-solvating plasticizers such as DIHP or BBP.

Following the gelation of the cast base plastisol, the white inner layer of the upright cone is cascaded down the preheated cone mold. Optimized gelation characteristics cause the inner layer of plastisol to gel at a consistent thickness from the top to the bottom of the mold. The plasticizer type and concentration significantly impact this gelation process, as well as end-use performance properties, such as modulus and low-temperature impact resistance. Preferred plasticizer systems are GP plasticizers such as DINP, often optimized with partial substitution of a lower-molecular-weight phthalate such as DIHP.

The outer cone layer is primarily decorative, providing the bright fluorescent reflective surface. But it must also be compatible with the inner cone and base plastisol layers and meet tough end use requirements. Like the inner-layer plastisol, the outer-layer plastisol must provide a uniform thickness by gelation as it cascades in a thin layer from the top to the bottom of the cone during the manufacturing process. The preferred plasticizer type is the same as that used in the inner plastisol layer.

7.5.8 FDA and Other Regulated Uses

Plasticized PVC must meet the Code of Federal Regulations (CFR), Title 21, for applications where there is contact with food. While the plasticizers—and other ingredients—would be considered “indirect” (i.e., nonintentional), they must still meet the specified food additive requirements. Rutkowski and Scala[41] published a summary of pertinent regulations and their application to plasticizers; the information contained therein remains applicable today. It lists the specific plasticizers sanctioned for use in various applications. Table 7.20 summarizes the CFR 21 Parts and Sections that apply to typical plasticizer applications, and some of the plasticizers reported as approved under these Federal regulations.

TABLE 7.20 Code of Federal Regulations (CFR) Title 21: Parts and Sections Relating to Plasticizer Applications[a]

	Indirect Food Additives							
	Adhesive Coatings and Components		Paper and Paperboard Components		Polymers			
Plasticizers	175.105 Use with Adhesives	175.300 Use in Coatings	176.170 Use with Aqueous and Fatty Foods	176.180 Use with Dry Foods	177.1210 Closures for Food Containers	177.2600 Rubber Articles for Repeated Use	Adjuvants, Production Aids, and Sanitizers: 178.3740 Plasticizers in Polymeric Substances	Specific Prior Sanctioned Food Ingredients: 181.27 Plasticizers
DBP[b]	•	•	•			•		
DnHP[c]	•	•	•		•	•	•	
DOP (DEHP)[b,c]	•	•	•	•	•	•		•
DIOP[d]	•	•				•		•
DOA[b]	•	•	•	•	•	•	•	
79A[c]	•		•		•		•	
DINP[d]		•	•		•	•	•	
DINA[d]		•	•		•	•	•	
DIDP[d]	•	•			•	•		
DPHP[c]	•	•			•	•		

(*Continued*)

TABLE 7.20 *Continued*

	Indirect Food Additives							
	Adhesive Coatings and Components		Paper and Paperboard Components		Polymers			
Plasticizers	175.105 Use with Adhesives	175.300 Use in Coatings	176.170 Use with Aqueous and Fatty Foods	176.180 Use with Dry Foods	177.1210 Closures for Food Containers	177.2600 Rubber Articles for Repeated Use	Adjuvants, Production Aids, and Sanitizers: 178.3740 Plasticizers in Polymeric Substances	Specific Prior Sanctioned Food Ingredients: 181.27 Plasticizers
DOTP[b]					•			
Citroflex® A-4[e]	•	•	•		•			•
BBP	•		•	•			•	
DINCH (approvals pending)[c]								

[a] Note that some of the approvals limit the level of plasticizer, type of materials, and the types of foods where these products can be used. This table should be used as a *guide*. It is the formulator's responsibility to ensure the proper usage for each of these plasticizers as well as other additives. Additionally, some approvals listed above are referenced to approval listings under Section 178.3470.

[b] Eastman Chemical Company, "Using *Eastman* Plasticizers Under Current FDA Food Additive Regulations," March 2003.

[c] BASF Corporation, "Plasticizers for Food Packaging and Handling Applications," December 2005.

[d] ExxonMobil Chemical, "Jayflex® Plasticizers Regulated Applications," 2002.

[e] Morflex technical bulletin data.

Clear, flexible vinyl films used for meat and produce wrap typically contain about 30 phr DOA plasticizer; other aliphatic dibasic acid esters are also allowed for this use, but are less cost-effective; these are linear alkyl adipate 79A, the straight-chain di-n-octyl, decyl adipate (810A or NODA), or the branched-chain adipate DINA.

The following is a typical flexible PVC food film starting formulation:

PVC (K71)	100
DOA	22
ESO	3
Ca/Zn stabilizer	2.5
Stearic acid	0.25
Antifogging agent	2–4

In addition to food wrap films, flexible PVC is applied as can end sealants, crown and closure gaskets, food processing belts, and milk and beverage tubing as defined in “3A Sanitary Standards for Multiple-Use Plastic Materials Used as Product Contact Surfaces for Dairy Equipment, Number 20-12,” issued by the United States Department of Agriculture (USDA). These PVC products use plasticizers that are sanctioned in CFR, Title 21. Epoxidized soy bean oil is also finding greater use in beverage sealants, in spite of its greater tendency for exudation.

Articles used in potable water applications such as tubing are often approved under the National Sanitation Foundation (NSF) approvals such as NSF 61. Several plasticizers, including both DINP and DIDP, have been approved for use here under the NSF toxicity and analyses programs, provided that defined levels of extractability are not exceeded. In these tests, the finished articles are placed in water for the prescribed time periods and the water is analyzed for extractable components. Any detected chemical is measured against its defined toxicity profile.

In Europe, plasticizers such as DINP, DIDP, citrates, DOTP, and more recently DINCH are approved for use in films, coatings, and tubes made of plasticized PVC for transporting beverages, with certain restrictions that exclude foodstuffs containing alcohols, essential oils, and milk and dairy products. Some of these plasticizers have defined migration limits. Specialized plasticized PVC food films with high oxygen permeability for the packaging of fresh meat can use DOA, citrates, di-n-hexyl azelate, and now DINCH (provided the migration does not exceed 5 mg/kg foodstuff or food simulant). Here, the total plasticizer content in the PVC article is limited to a maximum of 22 percent.

Toy makers around the world have been using plasticized PVC to make their products for more than 50 years. In addition to being valued because of its safety record, PVC is preferred because of the high quality of the toys that can be produced. Many of these attributes cannot be duplicated with other polymer systems. This is especially true for toys produced in rotomolding processes. The U.S. Consumer Product Safety Commission conducted a 5-year study on DINP in vinyl toys, with two Chronic Hazard Advisory Panels reporting, and concluded that there is “no demonstrated health risk” and “no justification” for banning its use.

In spite of very favorable scientific reviews published in 2006 by the European Union (EU), in their risk assessments of DINP and DIDP,[42,43] political governing bodies within the EU decided to ban the use of the phthalates DINP, DnOP, and DIDP at concentrations exceeding 0.1 percent in toys and childcare articles that can be placed in the mouth, and to prohibit the use of DBP, DDP, and DOP in any toy or childcare article. More expensive plasticizers such as citrates, polymerics, adipates, and cyclohexanoates are starting to be used as phthalate alternatives in toy manufacturing.

Flexible PVC products for medical applications are controlled by a different process than the one controlling these products for the food contact area. Fabricated medical devices are exposed to extracting reagents defined by the U.S. Pharmacopoeia; the toxicological behavior of the extracting reagent, containing the extractables, is then characterized. Plasticizers such as DIHP, DOP, DIOP, DINP, DIDP, and 711P meet these requirements and are used in PVC examination gloves, hospital mattress covers, and so on. However, flexible PVC medical tubing, blood bags, intravenous (IV) bags, and dialysis equipment still use primarily DOP; this is due to its status under "Prior Sanction, CFR, Part 181.27". These DOP-plasticized products have made significant contributions to the extended life of humans, due to medical technology developed around the use of flexible PVC devices. Citrate esters, which are more costly than DOP, compare favorably to DOP performance in PVC blood-bag-type formulations; it is also reported that approvals are being sought for the use of DINCH in these types of applications. See also the discussion of regulatory constraints in Chapter 20.

7.5.9 Other Application Areas

The versatility of vinyl allows the application of a wide variety of formulations, processes, and end products. Following are some examples of additional vinyl plastic products.

Fishing lures are an example of the most highly plasticized vinyl product known. The process involves making a hot melt solution of about 15 weight percent PVC resin in the plasticizer. This mixture is then injection-molded (or it may be cast into appropriate molds) and allowed to cool, where upon it maintains the molded shape. The high level of plasticizer gives the lure the necessary flexibility to mimic the motion of various live baits such as minnows or shrimp or worms. The density of the fishing lure can be adjusted by using blends of phthalates and adipates; the desired oily feel can be enhanced by using less compatible plasticizers such as DOTP or by adding a mineral oil. The following is a typical fishing lure formulation:

PVC (dispersion resin)	100
GP plasticizer (DINP, DOP, or DOTP)	600
Mineral oil or secondary plasticizer	100
Ca/Zn stabilizer	10
ESO	20
Dye/pigment	As required

Plastisol dip-coated cloth gloves are useful industrial work gloves providing electrical insulation and resistance to industrial chemicals. The process utilizes a cloth glove lining supported by a mold. This is dipped into a plastisol bath and then oven-cured at high temperature. GP plasticizers such as DINP are commonly used. Often to improve processability, a faster-fusing plasticizer is added. The following is a possible starting place formulation:

PVC (dispersion K68)	100
DINP	75
DIHP	15
Viscosity diluent (TXIB)	20
ESO	5
Ca/Zn stabilizer	2
Adhesion promoter	As required
Pigments	As required

The rotomolded plastisol process is utilized to make playballs, toys, and other hollow objects. A predetermined amount of plastisol is charged into the hollow mold, and then the second half of the mold is secured in place. The plastisol is uniformly distributed inside the mold due to bidirectional rotation of the mold throughout the gelling and curing steps of the process under high temperature. Plasticizer selection is generally restricted to GP plasticizers, but often fast-fusing plasticizers such as DIHP or BBP are added. The following is a possible formulation for a PVC ball to be produced by rotomolding:

PVC (dispersion resin)	100
DINP	80
BBP	20
Pigments or dyes	0–6 as needed
Stabilizer	2.5

Plastisol molded rain boots bring together a combination of formulations and processes. The sole and heel parts are each cast in places and gelled, but not fused. The heel formulation contains a reactive liquid, such as trimethylol propane triacrylate, which crosslinks to form a hardened heel under the final fusion conditions. Following gelation of the sole and heel, the warm boot mold is filled with a plastisol in a slush molding process. A thin uniform layer of gelled plastisol forms on the inside wall of the boot mold; the mold is then emptied of the excess plastisol mass and subsequently proceeds through the high-temperature curing oven. In some processes, an interior lining of fleece, or similar material, is installed in the boot interior prior to the final gelation/fusion steps; this ensures a uniformly bonded interior lining.

The injection molding process is commonly used to make lower-cost rain boots and a specialty product known as "meat packer" boot, which must have resistance to extraction reagents such as brine, fat, and natural oils. Oil extraction resistance is accomplished through use of an alloy of DIDP-plasticized PVC with a polar polymer—such as ABS, crosslinked NBR, or chlorinated PE. Production speed for shoe production can be accelerated through use of lower-molecular-weight PVC resin and faster-fusing plasticizers; generally, fillers such as $CaCO_3$ are used at very low levels (if indeed at all), as these fillers will decrease the abrasion resistance. An adipate ester is often added to improve the shoe flexibility. The following is a typical flexible shoe sole formulation:

PVC (K64)	100
DOP	85
DOA	15
ESO	3
Ba/Zn stabilizer	3
Stearic acid	0.25

Extruded vinyl products vary in nature. Garden hose typically consists of an extruded core of recycled flexible vinyl, the composition of which is optimized with the addition of virgin resin and/or GP plasticizer and/or filler. The core extrudate may or may not be covered over with a reinforcing mesh, followed by an extruded outer coating for desired appearance and durability. Preference is usually for the lower-cost GP plasticizers.

The following is a starting point in the development of a PVC hose formulation:

PVC (suspension, K65–70)	100
GP plasticizer (DINP)	55
ESO	5
$CaCO_3$	10
Ca/Zn stabilizer	3
Stearic acid	0.3
Pigments	As required

Premium and specialty plasticizers are used for special performance requirements such as resistance to migration, marring, volatility, and failure under low-temperature conditions. Some of these extruded shapes—especially gaskets—utilize chemical blowing agents to provide low-density, foamed shapes. Extruded straps for lawn chairs, as well as other exterior products, are typically formulated with GP plasticizers plus antioxidants, UV absorbers, and fungicides.

Waterstop is extruded into a wide variety of sizes and cross-sectional shapes. Waterstop is a highly filled flexible PVC product designed to meet the rigorous engineering requirements of the U.S. Army Corps of Engineers Test CRD C-572-74; this requirement specifies high toughness, excellent low-temperature flexibility, and resistance to ozone, volatility, and water absorption. Preferred plasticizers are 610P, L9P, DIDP/DINA blends, and blends of L9P and DIDP.

Extruded vinyl refrigerator gaskets are specially formulated to resist plasticizer migration into the thermoplastic refrigerator door liner, which is usually thermoformed ABS or polystyrene. The PVC gasket may be foamed. It is usually combined with (or shaped over) a magnetic strip, which ensures an air-tight seal while precluding the need for a mechanical latch on refrigerator and freezer doors. Preferred plasticizers are typically polymeric plasticizers and trimellitates. Adipate ester blends can be used if very low-temperature flexibility is required.

Metal substrates, such as fencing, lobster nets, tool handles, and football face guards, are coated by preheating and then dipping the hot metal into a fluidized bed of PVC powder. A thin, uniform layer gels as a coating on the metal substrate, and is then passed through high-temperature curing ovens. The high-temperature process requires low-volatility plasticizers such as higher-molecular-weight phthalates, trimellitates, epoxidized oils, or polyesters. Specially formulated PVC—using suspension-grade PVC—are now being molded into finished parts by casting, slush, or rotomolding processes under conditions of high temperature and essentially no shear. Such processes had historically been limited to more costly plastisol formulations.

7.6 FUTURE OF PLASTICIZERS

Regulatory reviews have generally found phthalates to be safe for use in most current applications. However, the future of plasticizers and flexible PVC may be tied to the political arena and the responses of legislatures to environmental pressure groups. With the low levels of success in their attacks on PVC, the focuses of these activists have switched in recent years to PVC additives, in particular phthalate esters and heavy metal stabilizers. The primary issue with external monomeric plasticizers such as phthalates is that plasticizers are not chemically bound to the polymer. Thus, the same actions that yield a flexible product upon incorporation of the plasticizer into the polymer result in the plasticizers being able to leave the polymer system under certain conditions. In general, the more efficient a plasticizer is in making PVC flexible, the greater is its tendency to migrate.

The rate at which these plasticizers can leave the polymer system is a slow, diffusion-controlled process. Studies on PVC geomembranes and roofing products show that although plasticizer can slowly migrate into other materials, after more than 20 years of service, over 50 percent of the original plasticizer remains intact. Many of these products still have years of active service life remaining. Vinyl swimming pool liners can last more than 10 years. Here, predominate failure mechanisms include UV degradation or degradation from chemical or biological factors, rather than plasticizer loss (although this may be a contributory factor). In other areas, PVC building wire is expected to have a useful life of up to 40 years or more, since the plasticizer systems are based on permanent plasticizers. The images promoted by activists of plasticizers dripping out of PVC products like water from a sponge are misleading.

There have always been applications where greater permanence is needed, and polymeric plasticizers and natural oil-based products have filled this need for many years. For those applications where a phthalate ester did not work, the formulator has had available a number of different plasticizer choices, including citrates, terephthalates, adipates, azelates, trimellitates, phosphates, benzoates, and others, in addition to the polymeric plasticizers. In recent years, the growth area for new plasticizers has been with new monomeric plasticizers intended for sensitive applications such as bottle cap liners, toys, food films, and medical tubing.

Any new plasticizer that comes onto the market is expected to undergo very expensive and lengthy product testing. Literally tens of millions of dollars have been spent over the past years in the product testings of DOP (DEHP), DINP, and DIDP. Any new product intended for "sensitive" applications would need to undergo a high level of testing costs to ensure that it is safe for its intended applications. Thus, even higher product development costs are to be expected for any new plasticizer.

In 1943, it was estimated[44] that over 20,000 chemicals had been proposed as plasticizers since the concept of plasticization was first applied to nitrocellulose polymers in the mid-19th century. Certainly, that number exceeds 30,000 today. Of all of these proposed plasticizers, the class of phthalate esters still remains the top performing plasticizer classification, having the most favorable cost structure and the greatest level of utility. With this large number of proposed plasticizers, the resulting commercial activities, market development projects, and perhaps a thousand product launches over the past 75 years, it is highly unlikely that a completely new-to-the-market plasticizer will arise with general purpose utility matching both the performances and costs of some of the general purpose phthalate esters. At best, what can be expected is that someone will find a way to dust off old developments or copy older products, combine this with a newer technology element, and end up with something more costly and of lower performance, applicable only for a specialized application.

If future legislative action were to restrict the use of phthalates in most general purpose applications, the expectations are that the alternative plasticizer choices will yield lower-performing, yet more expensive, flexible PVC products. This change will open up additional opportunities for replacement of flexible PVC with alternative plastics. Fortunately, the probability estimated today for such legislative actions seems remote.

The relative toxicological characteristics of plasticizers have been studied for over 30 years in both the United States and Europe. Initially, the focus was on DOP (DEHP) and DOA (DEHA) because of their historical wide usage in many applications, including flexible PVC food films and medical devices, but this has expanded to several other phthalates. In recent years, a substantial database in this area has been developed for a variety of phthalates. A European trade association, the European Chemical Industry Federation (CEFIC), has summarized the known information, including numerous independent reviews, translating the impact of plasticizers on public health and the environment.[45] Overall, these reviews have found phthalates safe for use as intended.

One of the primary questions for consumers, is "Do phthalates cause cancer?" In humans, they do not. The initial concern was triggered by a 1982 study conducted by the National Toxicology Program (NTP), which found that life time exposures to high doses of DOP (DEHP) led to an increase in the incidence of liver tumors in rodents, with the conclusion that DOP is "reasonably anticipated" to cause cancer in humans.

The International Agency for Research on Cancer (IARC) followed, labeling DOP (DEHP) as a "possible carcinogen." (The IARC has since reclassified DOP as "not classifiable as to its carcinogenicity to humans.") Over the next 20 years, this question was addressed in numerous studies, looking at the mechanisms by which tumors develop in rodents and the applicability of those proposed mechanisms to humans. It was concluded that although phthalates may cause cancer in rodents, the mechanism by which this occurs is not relevant to humans. This conclusion was supported by both the IARC and the European Union. Phthalates are not genotoxic, not estrogenic *in vitro*, and do not induce asthma. Evidence for reproductive and developmental toxicity, including decreased sperm production in response to high doses of DOP (DEHP) administered to rats during pregnancy, has been observed. However, these effects are not observed with higher-molecular-weight phthalates (e.g., DINP), and are not observed when primates are exposed at extremely high dose.[46] As the mechanism for these effects is unknown, the susceptibility of humans remains in question. Phthalates are of low environmental concern, as they are not persistent, bioaccumulative, or toxic by present definitions.

In 1993, the toy industry and the U.S. Consumer Product Safety Commission (CPSC) agreed that DOP (DEHP) would be eliminated from soft teethers and rattlers. As a precautionary move, the toy industry elected to remove all phthalates from these articles. In December 1998, after being asked to ban all vinyl toys, the CPSC issued an initial report on DINP stating that "few if any children are at risk."[47] Similar conclusions were reached following a review of the safety of DINP in toys by a panel of experts chaired by former Surgeon General C. Everett Koop. In their 1999 report, the experts concluded that "DINP in toys is not harmful for children in the normal use of these toys."[48]

The CPSC recommended further study and convened a Chronic Hazard Advisory Panel (CHAP) to review the body of scientific data available for phthalates. The CHAP report, issued in 2001, found "minimal to non-existent risk of injury" for the majority of children.[49] The report added that there might be a risk to children who mouthed DINP-plasticized soft PVC toys for 75 minutes a day or more, day after day, for extended periods of time. In September 2002, after five years of study, the CPSC issued a report concluding that children who mouthed DINP-plasticized toys face "no demonstrated health risk" and denied the petition calling for the ban of vinyl in toys. Furthermore, the CPSC stated that "If DINP is to be replaced in children's products, the potential risks of the substitutes must be considered. Weaker or more brittle plastics might break and result in a choking hazard. Other plasticizers might not be studied as well as DINP."[50]

The European Commission spent even longer looking at phthalate esters. On April 13, 2006, after 10 years of data review and analysis of hundreds of reports and studies, the European Commission published their results for DINP and DIDP. For DINP, they concluded that DINP is "... unlikely to pose a risk for consumers (adults, infants, and newborns) following inhalation, skin contact or ingestion,"[42] stating that there is no need for any further measures to regulate the use of DINP. Similar statements were expressed for DIDP, reporting that DIDP poses no risk to either human health or to the environment from any current use.[43] The report for DOP

(DEHP) has yet to be issued, but the preliminary conclusions already presented for discussions are that DOP (DEHP) is safe for current use, that no risk measures are needed for the general population, but there might be concern for exposure of neonates to DOP (DEHP).

Similar results were published in 2003 by the NTP Center for the Evaluation of Risks to Human Reproduction (CERHR), with DINP and DIDP being reported as "minimal" or "negligible" concern. DOP (DEHP) was also reported as "minimal concern" for the general public; however, there was "serious concern" expressed for critically ill neonates, "concern" for infants under age one, and "some concern" for toddlers over one, and "concern" for male offspring of exposed pregnant women.[51]

Human exposures to several phthalates have been studied by the CDC in three different test programs. In the biomonitoring of urine samples for phthalates and phthalate metabolites to estimate human exposures to DBP, DOP (DEHP), DINP, and BBP, the levels of exposures seen were 500–40,000 times lower than the highest NOAEL (no observed adverse effect level) reported for each of the phthalates. DINP was not detected in most test subjects.[52] Thus the exposure of the general population to phthalates is well below the exposure levels found to produce adverse effects in rats.

But the debates continues. Political pressure regarding phthalates continues due to the activities of special interest groups, even though phthalates have been subject to extensive testing and numerous safety assessments. In general, these reviews have found phthalates safe for use in most applications. Although the EU scientists found no need to place restrictions on the use of DINP and DIDP, the EU legislature imposed a ban on the use of three phthalates—DOP (DEHP), DBP, and BBP—in the production of toys and prohibits the use of three plasticizers—DINP, DIDP, and DnOP—in babies' toys intended to be put in the mouth. (In Europe, BBP has a Category 2 classification for developmental effects and a Category 3 classification for fertility, but it is also noted that its use in everyday products does not pose a human health risk). Clearly, other than perhaps for medical devices intended for use with neonates, there are no reasons that a formulator should have concern about use of phthalate plasticizers except where it is expressly prohibited. Indeed, the reformulation with alternate, less-studied plasticizers could result in poorer product performance, or, worse, adverse health effects from use of a substance that lacks the safety record. After all, phthalates have a 60-year history of safe use.

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CHAPTER 8

Specialty Plasticizers

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Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

8.1 INTRODUCTION

Plasticizers are key ingredients and tools for the vinyl formulator. They are used to adjust the hardness (or softness) of compounds to application requirements for a multitude of flexible vinyl applications. In Chapter 7, the use of general purpose plasticizers was discussed. General purpose phthalates dominate the volume of plasticizers purchased every year and are most often selected for compounding flexible vinyl. General purpose plasticizers such as di-2-ethylhexyl phthalate or diisononyl phthalate provide an excellent set of performance characteristics and economy in use for most applications. Some applications, however, require performance that cannot be achieved by use of a general plasticizer alone. For example, applications such as flexible vinyl hose require resistance to oils and solvents. Vinyl compounds with general purpose phthalates are not the optimum choice for this application. General purpose phthalates are easily extracted by solvents such as hexanes. Polyester polymeric plasticizers would be a much better choice for these compositions.

Another example is that of vinyl used for resilient flooring, where a high speed of processing is desired. Resilient flooring is produced by plastisol spread coating. Gelation and fusion characteristics dictate the speed of production. Comparing the gelation and fusion temperatures of a plastisol containing a general purpose phthalate to one with a dibenzoate plasticizer, the plastisol with the dibenzoate plasticizer will have lower gelation and fusion temperatures. This enables increased speed of processing. Dibenzoate plasticizers have higher solvating power for vinyl than general purpose phthalates. An example of a dibenzoate plasticizer that will increase in speed is Benzoflex® 2088. Polymeric plasticizers and benzoate esters are two examples of specialty plasticizers used in vinyl compounds for specific applications.

Besides polymerics and benzoates, there are several other important classes of specialty plasticizers. Citric acid esters form another such class, as well as those of adipates, trimellitates, specialty phthalates, epoxidized soybean oil, and phosphates. All of these add value to vinyl compositions that general purpose plasticizers cannot. The focus for this chapter is on benzoates, polymerics and citrates. Not every benzoate, polyester polymeric plasticizer, and citrate ester will be catalogued in this chapter. An understanding of these plasticizers, how they function, and how to use them to advantage in formulation of flexible vinyl compositions is the desired outcome of the investment in reading time.

8.2 BENZOATE PLASTICIZER TECHNOLOGY

Benzoate plasticizers have been recognized since the 1940s as useful plasticizers for PVC. It was not until the mid-1950s, however, that benzoates useful in vinyl compositions were specifically identified and commercialized.[1] Benzoate esters can be produced by direct esterification, transesterification, via the acid chloride route, or Schotten–Bauman reaction. The current preferred method for most benzoate esters is via direct esterification, which is illustrated in the following reaction:

$$2 \text{ benzoic acid} + \text{glycol} \rightarrow \text{dibenzoate ester} + 2 \text{ water} \tag{1}$$

Details of the reaction chemistry are listed in the patent literature.[1–4]

8.2.1 Benzoate Ester Applications

Benzoate esters are used in the following applications:

- Latex adhesives based primarily on polyvinyl acetate and polyvinyl acetate copolymers
- Hot melt adhesives based on block copolymers and ethylene vinyl acetate copolymers
- Latex coatings
- Polyurethane compositions, both reactive and thermoplastic
- Polysulfide sealants and coatings
- Flexible vinyl compositions based on plastisol technology and other processing techniques

Flexible vinyl applications for benzoates range from resilient flooring to molding and dip coatings. As a class, benzoate esters are known as high-solvating plasticizers for flexible PVC applications. Their principal performance attribute in complementing general purpose phthalates is speed. There certainly are other attributes and performance characteristics, but speed of production is key to their utility in flexible vinyl.

8.2.2 Commercial Benzoate Esters

Monobenzoates and dibenzoates dominate the types of benzoates commercially available. The largest producer of benzoate esters is Velsicol Chemical Corporation; their trade name is Benzoflex®. Listed below are the various types of benzoate plasticizers manufactured by Velsicol:

- Benzoflex 9-88: dipropylene glycol dibenzoate. This dibenzoate is very versatile and is used in many applications in vinyl and other polymers.
- Benzoflex 9-88SG: dipropylene glycol dibenzoate. This is a special grade for reactive urethane applications.
- Benzoflex 2-45: diethylene glycol dibenzoate. Benzoflex 2-45 is a solid plasticizer sold primarily in blends with other dibenzoate plasticizers.
- Benzoflex S-358: triethylene glycol dibenzoate. This solid ester is sold only in blends with other benzoate plasticizers.

- Benzoflex 284: propylene glycol dibenzoate. This ester is a very good solvator. When compounded in vinyl, it has excellent stain resistance for resilient flooring applications. It also is useful in automotive sealant plastisols.
- Benzoflex 50: a blend of dipropylene glycol and diethylene glycol dibenzoate. This has uses in multiple applications in adhesives and vinyl.
- Benzoflex 2088: a blend of three dibenzoates (di- and triethylene glycol, and dipropylene glycol dibenzoates. This blend is unique and is a special grade used for multiple applications.[2,3]
- Benzoflex 1046: a blend of 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, benzoate/isobutyrate, and dibenzoate. This blend is used in vinyl applications for superior stain resistance in resilient flooring and also in automotive plastisol sealants requiring excellent paintability and resistance to migration for wet-on-wet automotive coating applications.
- Benzoflex 6000: a blend of the same esters as Benzoflex 1046 in different ratios. Benzoflex 6000 is used in the same applications as Benzoflex 1046.
- Benzoflex 354: 2,2,4-trimethyl-1,3-pentanediol dibenzoate. This ester is used for bleed resistance in plastisol inks for textile applications.
- Benzoflex 181: 2-ethylhexyl benzoate. The monobenzoates are used to control viscosity in plastisols.[4]
- Benzoflex 131: isodecyl benzoate. Benzoflex 131 is lower in volatility than Benzoflex 181 and is useful as a viscosity-reducing plasticizer.
- Benzoflex 352: 1,4-cyclohexane dimethanol dibenzoate. This benzoate ester is a high-melting-point plasticizer that is compatible with PVC and is useful as a processing aid.
- Benzoflex P-200: polyethylene glycol (molecular weight 200) dibenzoate. Benzoflex P-200 has limited utility in PVC, as the compatibility of this low-volatility plasticizer in PVC is not great.

Specification properties as well as typical properties are listed in Table 8.1.[5]

8.2.3 Vinyl Applications Overview

As was said earlier, benzoate esters as a class are high solvators for PVC. Each product, however, has additional performance attributes. Table 8.2 gives a summary of these attributes by product.[6–9]

Table 8.3 lists general performance characteristics of dibenzoates selected to illustrate relative performance. Table 8.4 lists the formulations used. General purpose phthalates are usually employed as the reference for comparison. However, the best comparison for dibenzoates in the phthalate family is butyl benzyl phthalate (BBP), which is a true high-solvating plasticizer.

Tables 8.5–8.8 list additional processability data on selected benzoate plastizers. Tables 8.5 and 8.6 are Brabender PlastiCorder® processability data; Tables 8.7 and 8.8 list fusion data.

Figures 8.1–8.3 illustrate idealized traces with point references.

TABLE 8.1(*a*) Benzoate Plasticizer Specifications and Properties

	Benzoflex 9-88	Benzoflex 2-45	Benzoflex 50
Specifications			
Acidity (as benzoic acid) (%)	0.1	0.1	0.1
Appearance	Clear liquid, free of particulates	Clear, free of particulates	Clear liquid, free of particulates
Assay (as benzoate ester) (%)	98	98	98
Color, max. (APHA)	100	100	100
Hydroxyl number, max. (mg KOH/g)	15	15	15
Moisture, max. (%)	0.1	0.1	0.1
Typical Properties			
Assay (as benzoate ester) (%)	98.5	98.5	98.5
Boiling point at 5 mmHg (°C)	232	240	233.84
Color (APHA)	60	40	50
Density at 25 °C (lb/gal)	9.346	9.8	9.6
Dielectric constant at 60 Hz	7.6 (7.5 at 1 kHz)		
Dielectric constant at 10 Hz		7.16	
Flash point, COC (°C)	199	199	200.56
Freezing point (°C)	−40		<16
Freezing point two crystal forms (°C)		16, 28	
Melting point (°C)		28	
Moisture (%)	0.07		
Molecular weight, theoretical	342.3		
Molecular weight, typical		314.3	328
Odor	Mild, ester-like	Mild ester	Mild ester-like
Pour point (°C)	−19		−21
Refractive index at 25 °C	1.5282	1.5424	1.535
Specific gravity at 25 °C	1.12	1.178	1.146
Vapor pressure at 25 °C (mmHg)	2.29×10^{-27}	5.18×10^{-6}	2.29×10^{-7}
Volume resistivity (ohm cm^2/cm)	1×10^{10}		
Solubilities			
Aliphatic hydrocarbons and aromatic hydrocarbons		Soluble	Soluble
Solubility in water at 25 °C (%)	<0.01	<0.01	
Water solubility at 25 °C (%)	0.25	1	
n-Octanol			Insoluble
Water			Insoluble

TABLE 8.1(*b*) Benzoate Plasticizer Specifications and Properties

	Benzoflex 2088	Benzoflex 131	Benzoflex 181
Specifications			
Acidity (as benzoic acid) (%)	0.1	0.05	0.1
Appearance	Clear, free of haze and particulates	Clear, oily liquid	Clear liquid
Assay (as benzoate ester) (%)	98	98	98
Color, max. (APHA)	40	75	40
Hydroxyl number, max. (mg KOH/g)	8	4	
Moisture, max. (%)	0.1	1	0.1
Typical Properties			
Autoignition temperature (°C)			398 (748 °F)
Coefficient of thermal expansion (cm)			0.00072
Boiling point, at 5 mmHg (°C)		161	
Color (APHA)		10–40	
Density at 25 °C	1.1598		
Density at 25 °C (lb/gal)	9.66	7.92	
Dielectric breakdown voltage (kV)			40
Fire point, COC (°F)	480		
Flash point, COC (°C)		174	164.4
Flash point, COC (°F)	436		328
Freeze point (°C)	<16		−75
Heat of combustion (BTU/lb)			15,695
Glass point (°C)		−70	
Melting point (°C)		<−25	
Moisture (%)	0.07		
Molecular weight, theoretical	332		
Molecular weight, typical		262	
Odor	Mild ester	Ester-like	
Pour point (°C)			<−57
Pour point (°F)	−25		
Refractive index at 20 °C	1.5399		1.489
Refractive index at 25 °C		1.4878	
Specific gravity at 25 °C/25 °C		0.95	0.962
Surface tension at 25 °C (dyn/cm)	43.8		
Thermal expansion coefficient at 25 °C ($°C^{-1}$)	0.00076		
Viscosity at 23 °C (mPa s)			8
Viscosity at 25 °C (cP)		15	

TABLE 8.1(*c*) Benzoate Plasticizer Specifications and Properties

	Benzoflex 354	Benzoflex P-200	Benzoflex 6000
Specifications			
Acidity (as benzoic acid) (%)	0.1	0.1	
Acid number, max. (mg KOH/g)			0.3
Appearance	Clear liquid	Liquid, pale color	
Assay (as benzoate ester) (%)		98	
Color, max. (APHA)	150	100	125
Moisture, max. (%)	0.1		0.1
Specific gravity at 25 °C/25 °C (range)	1.070–1.090		1.015–1.021
Typical Properties			
Acidity (mEq/g)	0.02		
Appearance	Clear liquid		Light yellow oily
Assay, min. (%)	95		
Boiling point (°C)			280
Boiling point at 1 mmHg (°C)		217	
Boiling point at 55 mmHg (°C)	225.0–227.0		
Color (APHA)	150		
Dibenzoate, max. (%)			20
Flash point (°C)	212		
Flash point, closed cup (°C)			
Flash point, COC (°C)		>93.3	
Freezing point (°C)	Glass at −12	−30	
Melting point (°C)		28	
Moisture (%)	0.1		
Molecular weight, typical		408.2	
Odor	Mild ester	Mild ester	Ester-like
Refractive index at 25 °C	1.527–1.605	1.5252	1.485
Specific gravity at 25 °C/25 °C	1.07–1.09	1.17	1.04
Vapor pressure at 20 °C (mmHg)	0.00000518	$\ll 1$	
Viscosity at 25 °C (cP)	406	~75	
Viscosity at 50 °C (cP)	52		

The following conclusions can be drawn from the data listed in Tables 8.3–8.8 and in the references:

1. Dibenzoates are better solvators than general purpose phthalates, resulting in:
   - Lower plastisol gel and fusion temperatures. This translates to faster production in applications such as resilient flooring, molding, dip coating and vinyl leather cloth.
   - Higher plastisol viscosities
   - Fast dry blending and fusion times as illustrated by the PlastiCorder data
   - Lower relative fusion temperatures

TABLE 8.1(*d*) Benzoate Plasticizer Specifications and Properties

	Benzoflex 1046	Benzoflex 352	Benzoflex 9-88 SG
Specifications			
Acidity (as benzoic acid), max (%)		0.2	0.1
Acid number, max. (mg KOH/g)	0.2		
Appearance		White solid flake	Clear liquid, free of particulate
Assay (as benzoate ester) (%)			99
Assay (ester content), min. (%)		98	
Color, max. (APHA)	90		120
Color (10% in acetone), max. (APHA)		50	
Hydroxyl number, max. (mg KOH/g) (range)		15	4.0–6.0
Moisture, max. (%)	0.1	0.1	0.07
Specific gravity at 25 °C/25 °C (range)	1.021–1.034		
Typical Properties			
Acid number (mg KOH/g)	0.1		
Appearance	Colorless to light yellow oily liquid		
Boiling point at 5 mmHg (°C)	280		232
Brookfield viscosity at 25 °C (cP)	65		
Color (APHA)	70		60
Density at 25 °C (lb/gal)			9.346
Dielectric constant at 60 Hz			7.6 (7.5 at 1 kHz)
Ester content (%)	99.9		
Flash point, COC (°C)	177	258	199
Freezing point (°C)			−40
Melting point (°C)		118	
Moisture (%)			0.07
Molecular weight, theoretical			342.3
Molecular weight, typical		352	
Odor	Ester-like	Slight	Mild, ester-like
Pour point (°C)	−34		−19
Refractive index at 25 °C	1.492		1.5282
Specific gravity at 25 °C/25 °C	1.028		1.12
Specific gravity, solid at 25 °C		1.1363	
Vapor pressure at 25 °C (mmHg)			2.29×10^{-7}
Volume resistivity (ohm cm^2/cm)			1×10^{10}

TABLE 8.2 Benzoflex Vinyl Application

Benzoate Ester	Recommended Application	Performance Advantage
Benzoflex 9-88 dipropylene glycol dibenzoate	Plastisol, calendering	High solvator, UV light and heat stability
Benzoflex 284 propylene glycol dibenzoate	Plastisol, resilient flooring	Stain resistance
Benzoflex 50 DPG/DEG dibenzoate blend	General plastisol, other vinyl	High solvator, UV light and heat stability
Benzoflex 2088 DEG/TEG/DPG dibenzoate blend	Resilient flooring, foam	High solvator, UV light and heat stability
Benzoflex 131 isodecyl benzoate	Plastisol	Viscosity reduction
Benzoflex 181 2-ethylhexyl benzoate	Plastisol	Viscosity reduction
Benzoflex 354 trimethyl pentanediol (TMPD) dibenzoate	Plastisol, screen ink, sealants	Bleed resistance, solvator
Benzoflex 6000 TMPD diisobutyrate, dibenzoate, isobutyrate/benzoate blend	Plastisol, resilient flooring, auto sealant	Low bleed, low viscosity, stain resistance
Benzoflex 1046 TMPD diisobutyrate, dibenzoate, isobutyrate/benzoate blend	Plastisol, resilient flooring, auto sealant	Low bleed, low viscosity, stain resistance
Benzoflex 352 cyclohexane dimethanol dibenzoate	Plastisol	Thixotrope, good solvator

2. Physical performance compared with general purpose phthalates:
   - Better stain resistance in vinyl
   - Higher tensile strength
   - Higher modulus
   - Not as effective in low-temperature applications
   - Better extraction resistance to solvents and oils
   - Less resistance to extraction by water and water solutions
3. Compared with higher-solvating phthalates (BBP, DBP, DIBP, and DIHP), dibenzoates have:
   - Similar to better solvating capabilities
   - Similar to better stain resistance
   - Similar to better heat and UV light stability

These sets of performance properties suggest several flexible vinyl applications. Most of these are plastisol-based. To highlight and illustrate performance, the following examples are presented.

TABLE 8.3 Benzoate Performance In Plastisols

	Benzoflex 131	Benzoflex 284	Benzoflex 9-88	Benzoflex 50	BBP	DOP	7-11	TXIB
Processability Parameters								
Plastisol gel temperature (°C)	59	56	59	55	54	75	71	62
Foam factor/break time (s)	—	18/700	13/700	22/400	13/300	—	11/30	—
Vinyl heat stability (min)	6	6	5.5	5	4.5	6	7	6
Brookfield LVT Viscosity, 12 rpm at 23 d/c (P)								
1-day	7.1	64	104	58	114	98	52	7.3
7-day	8.6	98	138	123	169	133	74	9.3
14-day	8.8	120	155	133	188	151	93	7.2
28-day	8.3	153	154	150	222	166	99	5.6
Ratio of 28/1-day viscosity	1.8	2.4	1.5	2.6	2.0	1.7	1.9	0.77
Brabender PlastiCorder Heat Rise Data								
Torque at gel point (m-g)	—	10	9	25	18	—	20	—
Temperature at gel point (°C)	96	60	66	62	67	75	98	102
Torque fusion peak (m-g)	2600	2840	2100	2160	2610	720	95	102
Temperature at fusion point (°C)	156	108	120	121	112	159	170	162
Torque at degradation point (m-g)	2200	590	680	710	630	400	520	2380
Temperature at, degradation point (°C)	214	191	204	192	196	198	203	212
Fusion/gel time (min)	—	9.4	9.3	10.0	6.3	—	202	—
Relative fusion point temperature (°C)	102	71	75	70	74	125	123	108
Compatibility Parameter								
Roll test, 3-day, 140 d/f	0	0	0		0	0	0	0
Loop test, 7-day, 23 °C	0	0	0		0	0	0	0

Efficiency Parameters							
Specific gravity at 25 °C	0.95	1.14	1.13	1.12	0.98	0.97	0.95
Tensile Properties, ASTM D-638							
100% modulus (psi)	840	970	1160	950	800	1050	910
Tensile at break (psi)	2140	2600	2600	2500	2400	2100	2170
Elongation (%)	320	360	350	360	440	330	310
Shore A hardness, 10 s	65	68	66	65	68	72	66
Permanence Parameters							
Activated charcoal, volatile loss at 70 °C, ASTM D-1203 modified:							
24 hours, net loss (%)	37	10	7	5	NT	4	40
72 hours, net loss (%)	48	25	12	9	NT	6	52
168 hours, net loss (%)	56	35	16	15	NT	7	58
Extraction Resistance, Net Loss ASTM D-1239 (%)							
Heptane, 24 hours, at 23 °C	NT	6	9	18	36	81	NT
Cottonseed oil, 24 hours, at 23 °C	NT	1	2	4	5	16	NT
1% soap, 24 hours, at 50 °C	NT	9	8	14	2	2	NT

Note: Formula: 100 PHR Geon® 121A, 70 PHR plasticizer, 3 PHR Mark® M. Refer to Figure 8.2 for idealized Brabender PlastiCorder fusion curve and to Table 8.7 for test conditions.

TABLE 8.4 Generic Vinyl Formulations

	Plastisol (Parts by Weight)	General Purpose (Parts by Weight)	Dry Blend (Parts by Weight)
Dispersion resin, $K = 72$	100	—	—
Suspension resin, $K = 70$	—	100	100
$CaCO_3$ filler	—	—	17.8 or 0 as specified
Plasticizer	70	70	55.1 or 30 as specified
Heat stabilizer	2	2	2

TABLE 8.5 Bradbender PlastiCorder Dry Blend Data

	Benzoflex 9-88	Benzoflex 284	Benzoflex 50	DOP	BBP
Trace Data					
Temperature at point of initial torque increase (°C)	61	53	59	70	55
Torque at point of initial torque increase (m-g)	17	17	16	10	18
Temperature at dry peaks (°C)	80	78	78	88	80
Torque at dry peaks (m-g)	57	58	60	62	53

Notes: (1) Refer to Table 8.4 for formulation. Plasticizer level is 30 phr. (2) See Figure 8.1 for trace and point identification. (3) Brabender PlastiCorder test conditions: 650 ml Sigma blade head; 400 g charge; 33 rpm; temperature range 35–120 °C; rise rate 2 °C/min; 0–500 mg scale, 1 s damping.

TABLE 8.6 Brabender PlastiCorder Dry Blend Data

Plasticizer in Dry blend	Inflection Temperature (°C)	Dry Peak Temperature (°C)
Benzoflex 2088	68	76
Benzoflex 9-88	72	76
DINP	83	98
DIDP	86	106
DINA	86	108
ATBC	78	92
DOP	80	100
BBP	71	76

Note: Refer to Table 8.5 for test conditions and point definitions.

TABLE 8.7 Brabender® PlastiCorder Trace Data; General Purpose Resin Formula

	Benzoflex 9-88	Benzoflex 284	DOP	BBP
Trace Data				
Temperature at rapid torque increase point (°C)	67	60	78	63
Torque at rapid torque increase point (m-g)	80	40	50	20
Temperature at fusion peak (°C)	105	99	109	101
Torque at fusion peak (m-g)	2670	2940	1920	2580
Torque after fusion (m-g):				
at 150 °C	920	720	810	930
at 160 °C	680	520	640	690
at 170 °C	490	380	440	480
Temperature at degradation (°C)	177	172	178	176
Torque at degradation (m-g)	350	350	360	420
Relative fusion temperature (°C)	80	73	90	77

Note: (1) Refer to Table 8.4 for formulation. (2) Refer to Figures 8.2 and 8.3 for trace point identification. (3) Brabender PlastiCorder test conditions: heat rise test, 2 °C/min; #5 roller head used with 50 g charge; temperature range 40–200 °C.

TABLE 8.8 Additional Brabender PlastiCorder® Fusion Curve Data

	Benzoflex 2088	ATBC	DINP	BBP	DINA
Torque Curve Points					
Peak temperature (°C)	108	115	116	108	147
Peak torque (m-g)	7850	6550	5850	8250	2000
Torque at 150 °C (m-g)	2700	2800	2700	2700	1975
Torque at 160 °C (m-g)	2200	2300	2250	2150	1875
Torque at 170 °C (m-g)	1700	1875	1850	1700	1625
Temperature Curve Point					
Inflection temperature (°C)	67	81	83	68	121

Notes: (1) Refer to Figures 8.2 and 8.3 for trace information. (2) Refer to Table 8.4 for the formulation (50 phr) and to Table 8.7 for test conditions.

8.2.4 Performance Examples and Formulations

- Resilient flooring
- Vinyl leather cloth
- Plastisol ink
- Automotive sealants.

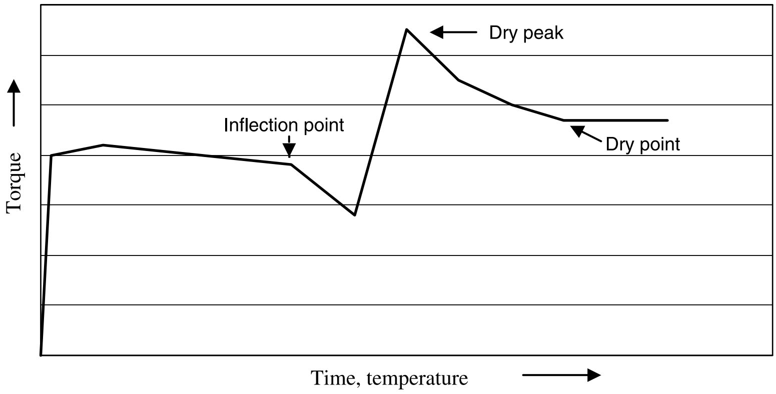

Figure 8.1 Brabender PlastiCorder dry blend heat rise curve.

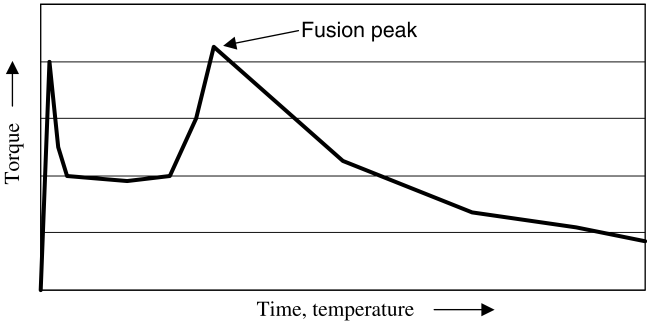

Figure 8.2 Brabender melt process generalized trace.

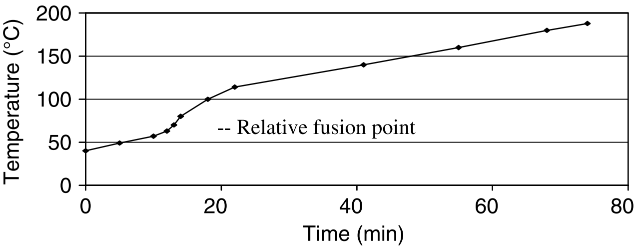

Figure 8.3 Brabender PlastiCorder relative fusion point.

8.2.4.1 Resilient Flooring High solvators have been used for many years in resilient flooring.[10–12] Depending on the region of the world, resilient flooring construction can be quite complicated. Figure 8.4 depicts an idealized European resilient flooring construction. A North American construction differs from the European in that the number of layers, as well as the base on which it is built, is significantly different. European constructs are built on glass mats, have a saturation layer for

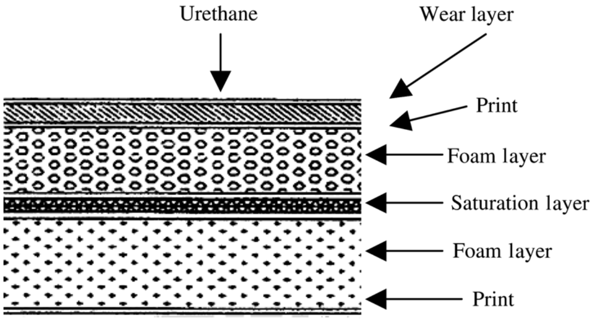

Figure 8.4 European flooring construction.

the glass mat, and have foam layers on both sides of the saturated mat. North American constructions are built on felt (latex-saturated fibrous material) and typically have one foam layer.

Table 8.9 lists starting or basic plastisol flooring formulations for the wear and foam layers as typically used in European products (note the use of organotin stabilizer in the topcoat wear layer). The main difference between North American and European formulations is that North American products often use only high-solvating plasticizers, whereas European equivalents tend to use a blend of general purpose phthalates and high solvators.

Tables 8.10 and 8.11 list data on basic wear and foam layers. Table 8.12 lists typical European wear layer formulations using Benzoflex 2088, and Table 8.13 lists data on these compounds. Benzoflex 9-88 and 2088 plasticizers were compared with BBP in the basic formulations. The basic wear and foam layer data listed indicate that the benzoates tend to give plastisols with somewhat higher viscosities than BBP (which will require reformulation in some instances), but better foam blow ratios and foam quality. In the European wear layer, the rheology of the dibenzoate-based plastisol is that required for the application. The staining characteristics were excellent.

TABLE 8.9 Basic Resilient Flooring Formulations

Topcoat Formulation		Foam Formulation	
phr	Raw Materials	phr	Raw Materials
100	PVC, D9-20	100	PVC, D2-22
44	Plasticizer	40	Plasticizer
1.4	Stabilizer (Sn)	1.5	Stabilizer (Ba/Zn)
2.4	ESO	5	ESO
		5	Carboxylic acid derivative
		10	Glycol diisobutyrate
		30	Calcium carbonate
		3	Azodicarbonamide
		3	Titanium dioxide

TABLE 8.10 Basic Topcoat Formulation Test Data

	BBP	Benzoflex 9-88	Benzoflex 2088
Brookfield viscosity, RVT, 20 rpm (Pa s):			
As prepared	11.5	18.1	15.6
1 day	17.7	25.3	23.5
3 days	25.3	26.9	25.3
Severs viscosity, as prepared (Pa s):			
10 psi	25.0	53.6	43.6
40 psi	45.2	99.8	88.9
80 psi	56.4	121.5	114.2
100 psi	57.8	125.2	122.0
Severs viscosity, 1 day (Pa s):			
10 psi	28.4	50.7	48.2
40 psi	52.5	95.8	95.7
80 psi	66.3	118.0	122.0
100 psi	70.7	123.4	128.4
Fusion volatility, (% weight loss):			
100 s	0.52 ± 0.10	0.46 ± 0.02	0.34 ± 0.01
150 s	1.21 ± 0.04	1.01 ± 0.13	0.67 ± 0.02
Charcoal volatility (% weight loss):			
As prepared	1.50 ± 0.05	2.29 ± 0.02	1.53 ± 0.05
1-day, ambient	1.85 ± 0.04	2.67 ± 0.04	1.85 ± 0.10
1-week, ambient	1.81 ± 0.14	2.51 ± 0.04	1.67 ± 0.04
Heat stability at 200 °C (yellowness index):			
Initial	5.4	6.7	7.1
5 min	14.1	15.8	16.8
7.5 min	23.6	27.0	29.6
10 min	36.6	42.3	48.3
Shore A hardness	79.0 ± 0.6	82.9 ± 0.7	79.4 ± 0.4
Low-temperature flexibility	−5 °C	1 °C	−4 °C
Stain resistance ratings, ΔE:			
Kiwi brown	84	66	86
Driveway sealant	7	6	7
1% oil brown	7	6	6

The formulations can be adjusted to have rheology and processing speed to match a range of production requirements.

8.2.4.2 Vinyl Leather Cloth Vinyl leather is very similar to flooring constructions, and is actually made in a similar manner.[13] Figure 8.5 illustrates the structure of a vinyl leather cloth. Table 8.14 lists the formulations for the solid vinyl and foam

TABLE 8.11 Foam Layer Test Data

	BBP	DPGDB	Benzoflex 2088
Brookfield viscosity, RVT, 20 rpm (Pa s):			
As prepared	6.7	6.8	7.9
1 day	18.3	11.3	13.6
3 days	23.2	14.0	17.2
Severs viscosity, 1 day (Pa s):			
10 psi	9.3	16.6	14.9
40 psi	21.6	41.8	37.0
80 psi	31.0	57.8	52.9
100 psi	33.9	61.7	58.9
Severs viscosity, 1 day (Pa s):			
10 psi	12.8	19.6	18.2
40 psi	26.5	473	44.6
80 psi	37.6	65.8	66.5
100 psi	41.7	71.1	71.2
Fusion volatility (% weight loss):			
100 s	5.19 ± 0.06	4.92 ± 0.19	4.45 ± 0.26
150 s	7.29 ± 0.15	6.43 ± 0.16	6.06 ± 0.12
Charcoal volatility (% weight loss):			
As prepared	6.89 ± 0.27	7.21 ± 0.21	6.30 ± 0.22
1 day	7.13 ± 0.07	7.37 ± 0.11	6.64 ± 0.03
Foam blow ratio–foam quality:			
90 s fusion	1.67–p	1.75–f	1.97–g
100 s	1.94–f	2.12–g/e	2.20–g/e
110 s	2.14–f/g	2.35–g/e	2.37–e
120 s	2.24–g	2.44–g/e	2.55–g/e
130 s	2.11–f/g	2.43–g	2.61–g/e
140 s	2.47–f/g	2.68–g	2.79–g
Heat stability during fusion/foaming (yellowness index):			
Initial gel	23.8	24.3	24.6
100 s heating	20.6	20.9	20.6
120 s	20.1	20.4	20.1
140 s	20.1	20.6	19.7
Foam heat stability at 200 °C (yellowness index):			
Initial	22.7	26	26.1
5 min heat time	34.2	33.8	31.9
7.5 min	48.7	48.6	43.5
10 min	57.1	57.2	53.9

TABLE 8.12 Resilient Flooring Wear Layer Formulations

	Formulation Number		
Raw Material (phr)	1	2	3
Lacouyl® PB1702 dispersion resin	85	100	70
Solvin® 266SF blending resin	15	0	30
Benzoflex® 2088	19.7	19.7	34.8
DINP	30.3	22.7	15.2
Trimethyl pentanediol diisobutyrate	0	7.6	15.2
Edenol® D81 ESO	4.5	4.5	4.5
Viscobyk® 5050 viscosity reducer	1.5	1.5	1.5
Mark® CZ 116 heat stabilizer	4.5	4.5	4.5

layers that make up the vinyl leather cloth. Table 8.15 lists benzoates such as Benzoflex 2088 that can be used to advantage in this type of application—again for speed and foam quality.

8.2.4.3 Plastisol Silkscreen Ink Plastisol screen ink is used to print on fabrics.[14] Typically, plastisol ink is used on T-shirts, sports apparel and the like. Two types of inks are commonly used: a general purpose type and a bleed-resistant type (known as "athletic white"). High solvators are used in these inks to improve the processing window to enable achievement of full physical properties under variable cure conditions. Benzoflex 354 is used in bleed-resistant ink. Table 8.16 lists a starting formulation for a low-bleed ink. Table 8.17 lists data.[15]

Figure 8.6 illustrates that Benzoflex 354 has very low bleed. It is compared with polymeric plasticizers, a general purpose plasticizer, and 2,2,4-trimethyl-1,3-pentanediol benzyl phthalate. Benzoflex 354 is also an excellent solvator, which is a further advantage for screen printing applications.

8.2.4.4 Automotive Plastisol Sealants Plastisol sealants are used to seal seams in automobiles.[16] The type of plasticizer required depends on where the seal is used, as well as the plastisol cure conditions. Benzoflex 1046, 2088, 284, and 131 have been used in this application. Table 8.18 lists a starting formulation for an automotive sealant.

8.3 POLYESTER POLYMERIC PLASTICIZERS

Different types of polymers can be used to plasticize PVC compositions. For example, nitrile rubber (NBR), thermoplastic polyurethane, and ethylene vinyl acetate(EVA) co- and terpolymers can be used to alloy with PVC. These types of compositions are discussed in Chapter 15. This section will focus on the class of polyester polymeric plasticizers. These have average molecular weights ranging from less than 1000 to about 25,000, and are viscous liquids to semisolids at room temperature.

TABLE 8.13 Resilient Flooring Wear Layer Data

	Formulation Number		
	1	2	3
Variable level (phr):			
Benzoflex 2088	19.7	19.7	34.8
DINP	30.3	22.7	0
TMPD diisobutyrate	0	7.6	15.2
Dispersion resin	85	100	70
Blending resin	15	0	30
Brookfield RVT viscosities at 23 °C (Pa s):			
Initial, 2.5 rpm	1.8	1.8	0.9
Initial, 20 rpm	1.8	1.6	0.9
24 hours, 20 rpm	2.1	2.3	1.1
3 days, 20 rpm	2.4	2.5	1.2
7 days, 20 rpm	2.3	2.7	1.3
TA rheometer:			
Gel temperature (°C)	107	105	96
Fusion peak (°C)	143	142	130
Severs viscosity at 23 °C (Pa s):			
Initial, 69 kPa	2.3	2.9	1.1
Initial, 276 kPa	2.3	3.3	0.7
Initial, 483 kPa	2.1	3.0	0.8
24 hours, 69 kPa	3.1	3.9	1.4
24 hours, 276 kPa	2.2	3.7	1.0
24 hours, 483 kPa	1.4	3.1	0.7
Tensile data:			
Temperature at max. (°C)	187	176	190
Tensile at max. (MPa)	17.9	18.7	16.2
100% modulus (MPa)	8.9	9.3	9.1
Elongation at max. temperature	299	302	258
Temperature at max. elongation (°C)	198	184	187
Activated charcoal volatility (% weight loss after):			
1 day	3	6	8
3 days	4	8	12
7 days	6	10	14
Stain resistance (visual ratings) to:			
1% oil brown dye	7	4	3
Brown shoe polish	6	5	3

(*Continued*)

TABLE 8.13 *Continued*

	Formulation Number		
	1	2	3
TA rheometer viscosity data at 25 °C (Pa s) at shear rates:			
Initial, 100 s^{-1}	2.38	2.39	0.86
Initial, 400 s^{-1}	2.14	2.62	0.63
Initial, 800 s^{-1}	1.94	2.18	0.62
24 hours, 100 s^{-1}	2.15	2.46	0.96
24 hours, 400 s^{-1}	1.94	2.69	0.69
24 hours, 800 s^{-1}	2.82	2.17	1.4
Foam factor (ml)	196	169	18
Time, foam break (min)	128	99	158
Heat stability (min)	61	61	50
Shore A, 10 s	73	74	71
QUV, 500 hours, ΔE	8.4	5.8	7.1

TABLE 8.14 Formulations for Vinyl Leather Cloth

Skin Layer		Foam Layer	
Ingredient	Parts	Ingredient	Parts
PVC dispersion resin (D4-22)	100	PVC dispersion resin (D2-22)	100
Plasticizer	65	Plasticizer	75
Epoxidized soybean oil (ESO)	5	ESO	5
Carboxylic acid derivatives	5	Azodicarbonamide (AZO)	2
Calcium carbonate	15	Zinc oxide	0.8
Ba/Zn stabilizer	3	Ba/Zn stabilizer	1.5
TiO_2	0	TiO_2	3

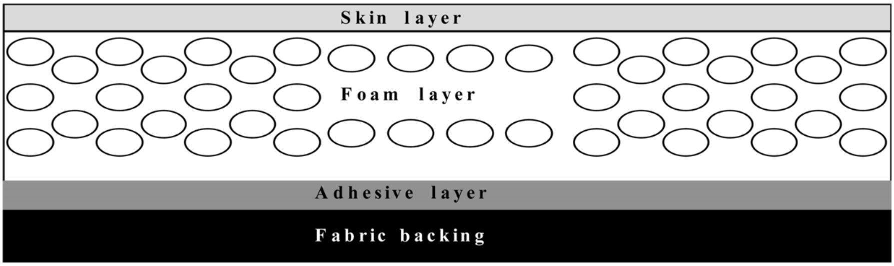

Figure 8.5 Vinyl leather cloth construction.

TABLE 8.15 Data on Fused Vinyl Skin and Foam Layers in Skin/Foam Construction

	Benzoflex 2088	Benzoflex 9-88
Skin Layer Data		
Tensile data, at break, ASTM D-638 (MPa)	20.6	21.5
Elongation (%)	470	450
100% modulus (MPa)	7.7	8.3
Shore A value, 10 s, ASTM D-2240	59	63
Low-temperature flex T_f (°C)	−30	−31
Volatility, ASTM D-1203, weight loss (%)	3.77	5.13
Heat stability at 200 °C, ΔE^1, after 10 min	34.4	34.1
20 min	52.0	60.3
30 min	61.6	65.6
40 min	67.4	66.5
Foam Layer Data		
Foam blow ratio	3.40	3.33
Foam cell quality	Good	Good

TABLE 8.16 Silk Screen Plastisol Ink Formulation: Low-Bleed White Type

Raw Materials	Parts by Weight (phr)	%
PVC dispersion resin	100.0	27.78
Plasticizer	82.5	22.92
Diluent plasticizer	27.5	7.64
Calcium carbonate filler	100.0	27.78
Titanium dioxide	50.0	13.88
Total	260	100.00

TABLE 8.17 Test Data on Plastisol Compounds

	Primary Plasticizer Used			
Test Parameter	Benzoflex 354	Admex 412	Santicizer 278	DIDP
Plastisol viscosity, Brookfield HAT, $T_{\text{spindles}} = 25$ °C (Pa s):				
Initial, 1 hour:				
10 rpm	8.4	4.4	8.7	2.6
20 rpm	5.6	3.1	5.8	1.6
24 hours:				
10 rpm	9.0	5.4	10.0	3.1
20 rpm	5.8	3.7	6.3	1.9
1 week:				
10 rpm	14.4	7.6	14.4	4.2
20 rpm	9.2	5.1	8.7	2.6
Plastisol gel temperature (°C)	70	84	71	89
Fabric bleed rating (total color change from white, ΔE)	9.6	14.5	16.7	21.0

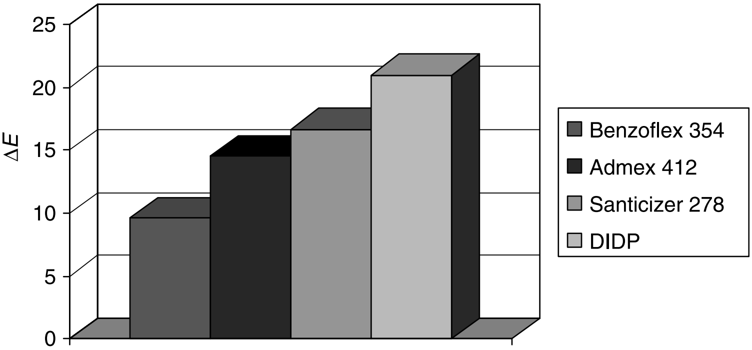

Figure 8.6 Bleed resistance of vinyl ink over red polyester blend.

TABLE 8.18 Benzoflex 354 Automotive Plastisol Sealant Formulation

Ingredient	phr
Dispersion resin	80
Blending resin	20
Whittaker 5963 $CaCO_3$	33
Whittaker 808 $CaCO_3$	67
DOP	50
Benzoflex 354	50
Euretek 580 adhesion promoter	4
Therm-Chek 1777 stabilizer	1

8.3.1 Properties of Polyester Plasticizers

Polyester polymeric plasticizers (or just simply polymeric plasticizers) are considered permanent plasticizers, and are used to compound vinyl requiring better performance than can be provided by monomeric plasticizers. Specifically, polymeric plasticizers are:

- *Resistant to migration into adhesives and other plastics in contact with vinyl.* Migration resistance to adhesives from vinyl is important for applications such as decals or electrical tapes. Monomeric plasticizers are not nearly as resistant to migration to adhesives on vinyl films as polymeric plasticizers.
- *Resistant to extraction by solvents and oils.* Polymeric plasticizers are much more resistant to extraction by solvents and oils than most monomeric plasticizers. General purpose phthalates are particularly poor in resistance to solvents compared with polymeric plasticizers. Polymeric plasticizers provide very significant improvements in performance for applications such as hoses used in contact with solvents or oils.
- *Resistant to migration to coatings or plastics.* Polymeric plasticizers are used in applications, such as gaskets for appliances, where resistance to migration, both to coatings and plastics such as ABS, are important. Properties of plastics into

which plasticizer has migrated can be destroyed; coatings can become sticky and unattractive.

- *Low in volatility.* Although polymeric plasticizers can have low-molecular-weight fractions that are as volatile as monomeric plasticizers, for the most part, polymeric plasticizers are relatively low in volatility. This is important in applications where it is necessary that there be little or no release of volatile organic compounds (VOCs) and where long-term retention of durability is desired.

The key property and the reason to use polymeric plasticizers is permanence. Polymeric plasticizers can be and are used as sole plasticizers when the greatest permanence is required.

The first polyester polymeric plasticizer developed in the United States was Paraplex® G-25, which was introduced in the early 1940s.[17] Paraplex G-25 is a very high-molecular-weight plasticizer that is essentially a solid at room temperature. It is still sold today. Since then, many more polymeric plasticizers have been introduced. Today, the total volume sold of polyester polymeric plasticizers is less than 150 million pounds worldwide. This number is very low compared with phthalates: about 13 billion pounds per year (2004).[18] While polymeric plasticizers are, as consumption figures suggest, significantly more expensive than general purpose phthalates, they exist because of the need for their performance characteristics.

8.3.2 Chemistry of Polyester Plasticizers

Polymeric plasticizers are prepared by reacting diols (glycols) with organic dibasic acids, usually in the presence of monobasic acids or alcohols. Normally, the reaction is direct esterification, but other approaches are possible to prepare polymeric plasticizers. The reaction is as follows:

$$\begin{aligned}&\text{diol} + \text{dibasic acid} + \text{monobasic acid/alcohol}\\&\quad\rightarrow \text{polyester plasticizer} + \text{water}\end{aligned} \tag{2}$$

In addition to the basic raw materials, catalysts are normally used, and an antioxidant may be added to the reactants. The reaction can be in solution or can be run in bulk (fusion). The ratios of the reactants control the molecular weight and, therefore, the properties of the polymeric plasticizer as well as the performance characteristics. The stoichiometry of polyesterification can be calculated via available software. It is possible to dial in molecular weight requirements and output ratios of ingredients.

Normally, end caps are used to control the molecular weight as well as plasticizer performance. There are some polymeric plasticizers available without them, but it is more common to use an end cap. When not capped, hydroxyl ends of polymeric plasticizers can generate problems with compatibility, especially under high-humidity conditions. Acid ends are also undesirable, as this also can affect the compatibility of the system as well as its heat stability. If the molecular weight of the polyester plasticizer is high, the level of end groups is minimal and this tends to mitigate the effect of not end-capping (in cases where that is desired).

The structure of the segments of the polymeric plasticizer control its performance in vinyl. Predictors used to assess the performance of simple or monomeric plasticizers can also apply to polymeric plasticizers if one considers the structure of the segments. There are certainly molecular weight effects, but performance really derives from ester type and content, with the aliphatic or aromatic nature of the segments providing a good clue as to the utility of any polymeric plasticizer. Understanding the constituents of a polymeric plasticizer will help to understand performance.

Listed below are diols and glycols that are commonly used to prepare plasticizers:

- *1,3-Butanediol.* This is a common diol used to prepare polymeric plasticizers. The single chain branch helps with compatibility with vinyl and lends a lower freezing point to the polyester.
- *1,4-Butanediol.* In the backbone of a polyester, this glycol will help low-temperature flexibility in vinyl, at the price of higher plasticizer freezing point and lower compatibility.
- *Neopentyl glycol.* In the backbone, this glycol provides excellent compatibility, weathering, extraction resistance, and electrical properties.
- *1,2-Propanediol.* This is one of the cheaper diols available. The branched chain allows for improved compatibility; it can be used with another diol to extend and improve performance and plasticizer properties.
- *2-Methyl-1,3-propanediol.* This is a new intermediate, and plasticizers based on it have recently been introduced into the market place. This diol, sometimes referred to as MP diol, can be used to replace neopentyl glycol. The performance advantages of neopentyl glycol are obtained, together with better low-temperature flexibility and more efficient plasticization.
- *Diethylene glycol (DEG).* This is used only in some specialty polyesters. Polymeric plasticizers based on DEG alone are far too polar for PVC and are not compatible. Mixed glycols with DEG have limited utility in vinyl.
- *1,6-Hexanediol.* This can be used, but has found limited utility.

The following dibasic acids are used to produce polymeric plasticizers:

- *Adipic acid.* The majority of polyester plasticizers are based on this versatile and relatively cheap C_6 dibasic acid. A good balance of efficiency, compatibility, and low-temperature flexibility are hallmarks of this acid.
- *Phthalic anhydride.* This dibasic anhydride is readily available, and low in cost. Phthalic acid in the backbone will enhance compatibility with PVC and extend the use of polyesters to more polar polymers. Also, the phthalic segment will promote fusion. There are, however, limits to its use. Polyesters with phthalic segments in the backbone are viscous and less efficient than corresponding adipates.
- *Azelaic acid.* This is a C_9 acid that yields polymerics with good plasticization efficiency and low-temperature properties in vinyl. Compatibility is acceptable for many applications.
- *Sebacic acid.* The first polyester plasticizer was based on sebacic acid, a C_{10} acid, and propylene glycol. It was not capped and had a very high molecular weight. Polymerics based on sebacic acid are efficient and provide excellent

low-temperature characteristics. Compatibility, however, with this acid is limited to higher-molecular-weight polymerics.

- *Glutaric acid.* This is a C_5 dibasic acid. Polymerics based on glutaric acid are similar to adipic-based polyesters, although they are less efficient than adipates.

In addition to a reaction diols with dibasic acids, most polyester polymeric plasticizers, as mentioned above, are end-capped. Organic monobasic end caps are normally saturated fatty acid types. Alcohol end caps are usually in the C_8 to C_{10} range. For several applications, it is desirable to "finish" the polymeric plasticizer and reduce the residual acid or hydroxyl content essentially to zero. Acetic anhydride is typically used to eliminate hydroxyl content.

Polyester polymeric plasticizer design is very much like vinyl formulating. While limited raw materials are available, many designs are possible, and these "formulations" and the process to make them are considered trade secrets in many instances. Listed below are typical recipes:[17]

- Low-molecular-weight polymeric plasticizers:
  - Poly(1,2-propylene adipate): $n = 4$, mixed fatty acid-terminated
  - Poly(1,2-propylene azelate): $n = 4$, palmitic acid-terminated
- Medium-molecular-weight polymeric plasticizers:
  - Poly(1,3-butylene azelate): $n = 8$, myristic/palmitic acid-terminated
  - Poly(1,2-propylene adipate): $n = 8$, C_8—C_9 alcohol-terminated, partially post-acetylated
  - Poly(1,3-butylene azelate): $n = 16$, 2-ethylhexanol-terminated
- High-molecular-weight polymerics:
  - Poly(1,2-propylene/1,4-butylene adipate): $n = 30$, myristic/palmitic-acid terminated
  - Poly(1,2-propylene sebacate): $n = 50$ (estimate), hydroxyl-terminated

Polymeric plasticizer quality is typically described by the following parameters:

- *Color*: APHA scale or Gardner scale.
- *Viscosity*: Brookfield or kinematic. Viscosity is a comparative indicator of molecular weight.
- *Hydroxyl number*: mg KOH/g. This is an important indicator of design quality and degree of reaction and has performance and compatibility implications.
- *Acid number*: mg KOH/g. This is a quality indicator; lower values are desired for vinyl applications.
- *Gel permeation chromatography (GPC) data.* While not typically considered specification properties, data from GPC traces are of interest—specifically, the average molecular weight, number average molecular weight and polydispersity. Figure 8.7 illustrates a typical GPC curve.

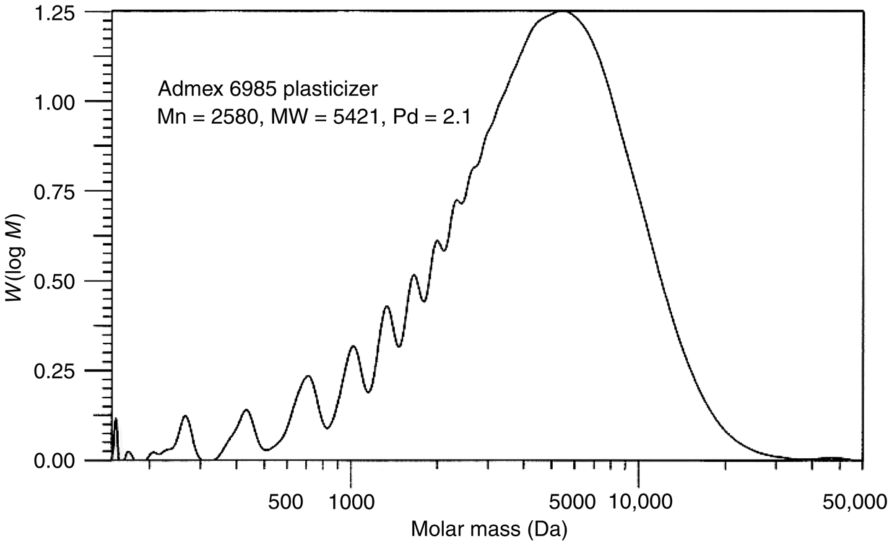

Figure 8.7 Typical polymeric plasticizer gel permeation chromatogram.

TABLE 8.19 Properties of Admex Low-Molecular-Weight Plasticizers

	Admex 522	Admex 523	Admex 525
Specifications			
Acid number, max. (mg KOH/g)	3	3	3.0
Appearance	Fluid to viscous liquid		
Hydroxyl number, max. (mg KOH/g)	25	25	30
Color, max. (Gardner)	3	2	3
Typical Properties			
Boiling point, at 5 mmHg (°C)		>315	>218
Color (APHA)	150	100	100
Color (Gardner)	1	1	1
Flash point, COC (°C)	241	238	282
Molecular weight, typical	757	1101	1943
Odor		Slight ester	Slight ester
Pour point (°C)	−21	−9	−9
Refractive index at 25 °C	1.503	1.514	1.461
Specific gravity at 25 °C	1.06	1.1	1.037
Vapor pressure at 20 °C (mmHg)		<0.001	<0.001
Brookfield viscosity at 25 °C (cP)	900	4400	350
Kinematic viscosity at 99 °C (cSt)	15	35	17
Acid number (mg KOH/g)	1.5	2.5	1.5
Hydroxyl number (mg KOH/g)	18	20	23
Appearance		Clear, viscous liquid	Clear, viscous liquid

TABLE 8.20 Specifications and Properties of Admex Low- to Medium-Molecular-Weight Plasticizers

	Admex 312	Admex 515	Admex 761
Specifications			
Acid number, max. (mg KOH/g)	1.5	3.0	4
Appearance	Light-colored liquid	Fluid to viscous liquid	
Hydroxyl number, max. (mg KOH/g)		20	5
Moisture, max. (%)	0.1		
Color, max. (Gardner)	2	2	3
Typical Properties			
Color (APHA)			25
Color (Gardner)		175	1
Fire point (°C)	313	246	268
Molecular weight, theoretical	2959	2522	4066
Odor	Mild		Mild ester
Pour point (°C)		35.2	−1
Refractive index at 25 °C	1.465	1.463	1.48
Specific gravity at 25 °C	1.0783	1.06	1.112
Vapor pressure at 20 °C (mm Hg)	<0.001		>0.0001
Volume resistivity (ohm cm^2/cm)		600	3650
Kinematic viscosity at 99 °C (cSt)	44	27	85
Acid number (mg KOH/g)	1.1	2	2.5
Hydroxyl number (mg KOH/g)		17	3
Saponification value	500		
Viscosity at 25 °C (cSt)	946		
Viscosity at 38 °C (cSt)	460		
Appearance			Fluid to viscous liquid

Tables 8.19–8.26 list typical specifications and properties of several of the Admex® line of polymeric plasticizers. This line is the consolidation of Huls America, Chemtura (Witco), and Union Camp (Caschem) polyester plasticizer products.

8.3.3 Performance of Polymeric Plasticizers in Vinyl

As indicated above, many combinations of raw materials are possible in different ratios. The different ratios will dictate structure as well as molecular weight. If the plasticizer is compatible (or reasonably so), the molecular weight is the most important consideration of relative performance in vinyl. Table 8.27 lists and Fig. 8.8 illustrates qualitative performance characteristics of polymeric plasticizers of all types.

Figure 8.9 illustrates the placement of the Admex plasticizer line in relation to molecular weight. Table 8.28 lists generic plasticizer vinyl performance data versus select

TABLE 8.21 Specifications and Properties of Admex Medium-Molecular-Weight Plasticizers

	Admex 1663	Admex 2632	Admex 409	Admex 334F
Specifications				
Acid number, max. (mg KOH/g)	2	2	1.5	2.0
Color, max. (APHA)		100	125	90
Hydroxyl number, max. (mg KOH/g)	15	25	28	28
Moisture, max. (%)			0.1	0.1
Color, max. (Gardner)	2			
Typical Properties				
Color (APHA)	100	55	125	100–125
Color (Gardner)	1	1		
Flash point, COC (°C)	249	285	>230	230
Moisture (%)			0.03	
Molecular weight, typical	3305	6116	6112	5828
Odor	Mild ester	Mild ester	Mild	Extremely low
Pour point (°C)	−26	4	3.5	3
Refractive index at 25 °C	1.463	1.465	1.4639–1.4669	1.4639–1.4669
Specific gravity at 25 °C	1.07	1.08	1.076–1.084	1.076–1.084
Vapor pressure at 20 °C (mmHg)			<0.1	<0.1
Brookfield viscosity at 25 °C (cP)	550	3320	3100–3800	3100–3800
Kinematic viscosity at 99 °C (cSt)	35	133	29–35	
Acid number (mg KOH/g)	1	1	1.00–1.50	1.0–2.0
Hydroxyl number (mg KOH/g)	7	20	22.0–28.0	22.0–28.0
Appearance	Yellow liquid	Fluid to viscous liquid	Pale yellow liquid	Light straw-colored liquid

TABLE 8.22 Specifications and Properties of Admex Low- to Medium-Molecular-Weight Plasticizers

	Admex 412	Admex 1723	Admex 6996
Specifications			
Acid number, max. (mg KOH/g)	2.2	3	2
Appearance			Bright, fluid to viscous liquid
Color, max. (APHA)	100	150	
Hydroxyl number, max. (mg KOH/g)		25	15
Moisture, max. (%)	0.07		
Color, max. (Gardner)	1	1	1
Typical Properties			
Color (APHA)	100	100	100
Color (Gardner)		1	1
Flash point, COC (°C)	188	274	249
Moisture (%)	0.07	0.02	
Molecular weight, typical	2265	2955	3305
Odor	Extremely low	Slight ester	Mild ester
Pour point (°C)	−20	−9	−26
Refractive index at 25 °C	1.430–1.460	1.475	1.463
Specific gravity at 25 °C	1.030–1.060	1.107	1.07
Vapor pressure at 20 °C (mmHg)	>0.1		
Brookfield viscosity at 25 °C (cP)	230–530	4800	550
Kinematic viscosity at 99 °C (cSt)	21	67	35
Acid number (mg KOH/g)	2.2	2	1
Hydroxyl number (mg KOH/g)	22.5	19–25	7
Appearance	Light straw-colored liquid	Clear, viscous liquid	

monomeric plasticizers. Tables 8.29–8.31 list vinyl data on select Admex plasticizers and other polymeric plasticizers. The data as a whole illustrate the relative performance and permanence of polymeric plasticizers. Not included in the comparison data is typical performance in plastisols. Polymeric plasticizers tend to be very viscous, and formulating plastisols to application viscosities can be difficult. Blends of polymeric plasticizers and monomeric plasticizers can be used (as is often the case always in plastisols), or solvents can be used to form organosols. Plastisol/organosol formulations are in the specific examples in the following.

8.3.3.1 Calendered Film for Electrical Applications Polymeric plasticizers are used in applications such as vinyl electrical tape due to their resistance to migration into adhesives, their long-term permanence, and their good electrical properties. Tape can be produced by several fabrication techniques. Calendering is an economic approach. Admex® 6996 and 312 were designed for this type of

TABLE 8.23 Specifications and Properties of Admex Medium-Molecular-Weight Plasticizers

	Admex 6969	Admex 6994	Admex 6995
Specifications			
Acid number, max. (mg KOH/g)	2	2	2
Appearance	Bright fluid to viscous liquid		Clear liquid
Color, max. (APHA)	100		
Hydroxyl number, max. (mg KOH/g)	25	5	10
Moisture, max. (%)			0.1
Color, max. (Gardner)		3	25
Typical Properties			
Boiling point at 5 mmHg (°C)			371
Color (APHA)	100	175	150
Color (Gardner)	1	1	20
Flash point, COC (°C)	279	535	248
Molecular weight, typical	4000	4977	3791
Odor	Mild ester		Mild ester
Pour point (°C)	−23	−18	−26
Refractive index at 25 °C	1.465	1.468	1.465
Specific gravity at 25 °C	1.09	1.05	1.09
Brookfield viscosity at 25 °C (cP)		3550	
Kinematic viscosity at 99 °C (cSt)		85	
Acid number (mg KOH/g)	0.5	1	1
Hydroxyl number (mg KOH/g)	18	3	5
Viscosity at 25 °C (cSt)	3000		2000
Viscosity at 99 °C (cSt)	100		60
Appearance	Clear to viscous liquid		

application, among others. These plasticizers have molecular weights of about 3000. Table 8.32 lists a starting formulation for this application. Table 8.33 lists performance data relating to this application. The excellent low-temperature and electrical properties, besides resistance to migration to adhesive migration that polymeric plasticizers in general provide, are important considerations for this application. Note also the low oil extraction of the plasticizer in this application.

8.3.3.2 *Extrusion Applications* Gaskets for refrigerator doors or hose applications require higher-molecular-weight polymeric plasticizers. Excellent extraction resistance, permanence, low odor, and migration resistance are required of plasticizers for these extruded applications. Admex® 6187 or 429 and 910.001 are examples of plasticizers that are useful. They have medium to high molecular weights. Table 8.34 lists a starting formulation and Table 8.35 lists data relating to these applications.

TABLE 8.24 Specifications and Properties of Admex Medium-Molecular-Weight Plasticizers

	Admex P-27	Admex 314	Admex 770
Specifications			
Acid number, max. (mg KOH/g)	2	30–35	3.5
Appearance	Light straw-colored liquid	Light-colored liquid	Fluid to viscous liquid
Color, max. (APHA)	125	150	125
Hydroxyl number, max. (mg KOH/g)	25		5
Viscosity, at 25 °C (Gardner)		Z-3–Z-4	
Color, max. (Gardner)			2
Typical Properties			
Color (APHA)	125	60	25
Color (Gardner)			1
Flash point, COC (°C)	>200	315	271
Moisture (%)	0.07	0.13	
Molecular weight, typical	6325	4943	5394
Odor	Mild	Mild	Mild ester
Pour point (°C)	10		−9
Refractive index at 25 °C	1.4600–1.4750	1.479	1.468
Specific gravity at 25 °C	1.090–1.120	1.192	1.11
Vapor pressure at 20 °C (mmHg)		<0.001	
Brookfield viscosity at 25 °C (cP)	4000–5000		4300
Acid number (mg KOH/g)	1.5	34	2.5
Hydroxyl number (mg KOH/g)	15.0–25.0		2
Fire point (°C)		338	
Saponification value		512	
Viscosity at 25 °C (cSt)		5000	
Viscosity at 99 °C (cSt)		150	
Appearance		Light-colored liquid	
Viscosity at 25 °C (Gardner)		Z3+	

Note the very low volatility for long-term permanence and low oil extraction of the polymeric plasticizer.

8.3.3.3 Plastisol and Organosol Applications As stated earlier, polymeric plasticizers are high in viscosity and are poor solvators. Polymerics are not easily formulated into plastisols. There are, however, certain applications requiring the permanence of polymerics. Lower-molecular-weight polymerics have been used in plastisols, but even the highest-molecular-weight polymerics can be formulated to provide suitable rheology. Admex 770 is well suited to decals for graphic applications (decals). Admex® 760 is very high in molecular weight and is also used for cast decals. Admex® 523 is low in molecular weight but also high in viscosity. It is

TABLE 8.25 Specifications and Properties of Admex Medium- to High-Molecular-Weight Plasticizers

	Admex 775	Admex 1667	Admex 300	Admex 6187
Specifications				
Acid number, max. (mg KOH/g)	2	3	2	2
Appearance	Fluid to viscous liquid	Fluid to viscous liquid	Light-colored liquid	Clear fluid to viscous liquid
Hydroxyl number, max. (mg KOH/g)	25	10		25
Moisture, max. (%)			0.1	
Color, max. (Gardner)	2	3	5	2
Typical Properties				
Boiling point at 5 mmHg (°C)	288	371		
Color (APHA)	125	150		50
Color (Gardner)	1	1	3	1
Flash point, COC (°C)	277	277	327	>260
Moisture (%)			0.03	
Molecular weight, typical	6137	5935	5457	6262
Odor	Mild ester	Mild	Mild	Mild ester
Pour point (°C)	−17.8	−26		−30
Refractive index at 25 °C	1.467	1.47	1.466	1.468
Specific gravity at 25 °C	1.11	1.12	1.099	1.095
Vapor pressure at 20 °C (mmHg)			<0.0001	
Brookfield viscosity at 25 °C (cP)	5000	6500	3300	5900
Kinematic viscosity at 99 °C (cSt)	165	190	117	170
Acid number (mg KOH/g)	0.5	2	0.5	1.5
Hydroxyl number (mg KOH/g)	17	7		15

used in foam from plastisols. Foams formulated from Admex 523 provide excellent sound-deadening characteristics. Table 8.36 lists a starting cast application for Admex 770, and Table 8.37 lists data developed on this formulation. The plastisol viscosities have been adjusted to values required for efficient processing. Table 8.38 lists a starting foam formulation.

8.3.3.4 Calendered Films for Packaging, Decals, and Related Applications Decals are also made from calendered films, as well as a variety of products, including packaging. The ability to print these films with waterborne

TABLE 8.26 Specifications and Properties of Admex Medium- to Higher-Molecular-Weight Plasticizers

	Admex 6985	Admex 429	Admex 330	Admex 760
Specifications				
Acid number, max. (mg KOH/g)	2	1.5	2	4
Appearance	Clear fluid to viscous liquid	Light straw-colored liquid	Light-colored liquid	Clear fluid to viscous liquid
Color, max. (APHA)		100	150	
Hydroxyl number, max. (mg KOH/g)	25	25		18
Moisture, max. (%)		0.07	0.1	
Color, max. (Gardner)	1			3
Typical Properties				
Boiling point at 5 mmHg (°C)	>287			>370
Color (APHA)	70	100	80	200
Color (Gardner)	1			1
Flash point, COC (°C)	277	200	291	302
Moisture (%)		0.07	0.07	
Molecular weight, typical	6508	6258	6437	13,500
Odor	Mild ester	Extremely low	Mild	Mild
Pour point (°C)	4	−18		1.67
Refractive index at 25 °C	1.466	1.460–1.475	1.466	1.47
Specific gravity at 25 °C	1.08	1.08–1.110	1.088	1.13
Vapor pressure at 20 °C (mmHg)		>0.1	<0.001	>0.0001
Brookfield viscosity at 25 °C (cP)	5250	4300–6600	3300	
Kinematic viscosity at 99 °C (cSt)	180			
Acid number (mg KOH/g)	1	1.5	1.2	3
Hydroxyl number (mg KOH/g)	18	18.0–25.0		15
Fire point (°C)			318	
Saponification value			501	79,250
Viscosity at 25 °C (cSt)			5300	
Viscosity at 38 °C (cSt)			2300	1300
Viscosity at 99 °C (cSt)			188	
Appearance			Light color viscous liquid	
Iodine value			<1.5	

TABLE 8.27 Relative Performance of Polymeric Plasticizers

				Resistance to		
Molecular Weight Class	Viscosity at 25 °C (cP)	Efficiency	Low-Temperature Properties	Hydrocarbons	Aqueous media	Migration
Low	250–1000	G	G	F	F	P–F
Medium–low	1000–3000	G	G	G	G	F–G
Medium	3000–12,000	G	G–F	G–VG	G–VG	G–E
High	25,000–250,000	G–F	G–F	E	F–E	E
Ultrahigh	Gum or powder	P	P	E–S	E–S	E–S

Rating scale: S = superior; E = excellent; VG = very good; G = good; F = fair; P = poor.

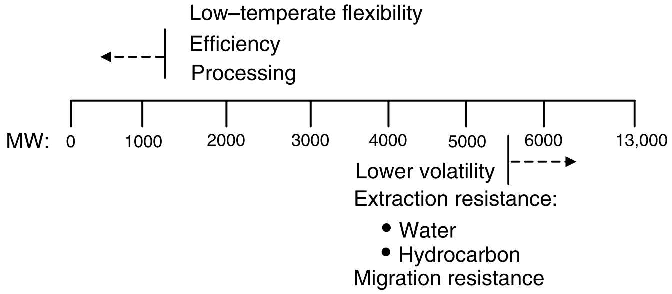

Figure 8.8 Effect of plasticizer molecular weight on performance. Plasticizers are chosen based on product requirements.

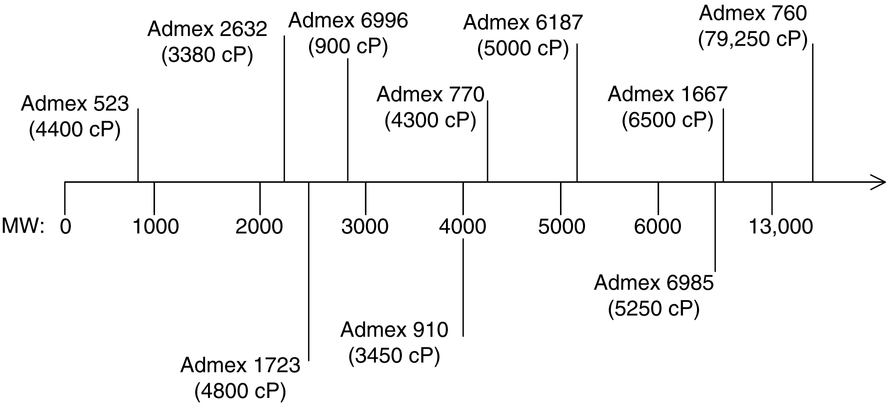

Figure 8.9 Molecular weight range of Admex plasticizers.

ink is an important consideration. Printing with waterborne inks requires that the vinyl has a high surface energy. Polymeric plasticizers such as Admex 6985 will yield films with high surface energy and excellent permanence. Table 8.39 lists a staring formulation, and Table 8.40 lists data. The surface energy of vinyl with Admex 6985 in such recipes is high—high enough to print with water-based inks.

8.3.4 Examples of Other Polymeric Plasticizers

In the first edition of this handbook, there were several starting formulations of interest. These formulations and some test results are listed in Tables 8.41–8.44.

8.3.5 Polymeric Plasticizer Suppliers

Globally, there are many producers of polymeric plasticizers. In the United States, there are three producers: Velsicol Chemical Corporation, Cognis (Henkel), and C.P. Hall Co. Velsicol Chemical purchased the Huls America line of polymeric

TABLE 8.28 Effects of Plasticizer Structure on Performance

	Plasticizer							
	A	B	C	D	E	TOTM	DOP	DOA
Parameter								
Molecular weight	10,000	8,000	5,000	950	850	546	390	371
Dibasic acid[a]	AD	SB	AD	AD	AD	TM	PA	AD
Termination[b]	OH	OH	FA	FA	FA	—	—	—
Viscosity at 25 °C	Gum	2200	900	2.8	39	2.2	0.5	0.1
Fusion temperature:								
°F	—	360	351	367	332	352	329	339
°C	—	185	177	186	167	178	165	171
Performance at 67 phr[c]								
Clash–Berg T_f (°C)	10	−12	−14	−23	−1	−29	−35	−60
Activated carbon volatility[d]	0.5	0.6	0.8	1.2	0.8	0.6	8.6	19.5
1% soapy extraction[e]	1.4	0.3	3.8	2.4	2.5	0.2	8.0	15.8
Hexane extraction[f]	0.3	0.2	2.8	14.3	1.8	33.9	33.5	34.0
PCE extraction[g]	2.5	12	19	25	25	38	38	38
Rubber migration[h]	0.1	0	1.3	6.7	2.3	8.7	13.0	24.5
Polystyrene mar[i]	None	None	None	Def.	Def.	Def.	Very bad	Very bad

[a] AD = adipic acid; SB = sebacic acid; TM = timellitic acid; PA = phthalic acid.

[b] OH = hydroxyl-terminated; FA = fatty acid-terminated.

[c] Formulation: PVC = 100, plasticizer = 67, stabilizer = 1.5 parts.

[d] 24 hours at 90 °C, ASTM D-1203.

[e] 24 hours at 90 °C, ASTM D-1239.

[f] 2 hours at 23 °C, ASTM D-1239.

[g] 2.5 hours at 23 °C, ASTM D-1239.

[h] 7 days at 60 °C, weight % lost, 10 mil, foam rubber, 0.25 psi.

[i] 48 hours at 70 °C, rating as above.

TABLE 8.29 Performance of Lower-Molecular-Weight (by Viscosity) Polymeric Plasticizers

Trade Name	Shore A Hardness	Clash–Berg, T_f (°C)	Activated Carbon (Vol %)	Extraction		Rubber Migration	Spew		FadO-Meter, hours or crack
				Soap	Hexane		%	Days to	
Admex 522	74	−10	4.3	8.5	9.3	—	0	280	250
Paraplex G-30	77	−11	1.3	3.5	2.8	5.0	0	180	1000
Paraplex G-50	75	−14	1.1	7.2	2.4	1.4	0	11	400
Paraplex G-51	72	−13.5	1.4	7.6	2.4	0.6	0.1	24	400
Paraplex G-31	83	−2	1.0	3.4	1.0	2.8	0	30	900
DOP control	68	−35	8.6	8.0	30	13	0.2	≥300	400

TABLE 8.30 Performance of Low- to Higher-Molecular Weight Polymeric Plasticizers

	Admex						
	523	761	910	770	775	760	Control DOP
Shore A hardness	99/97	97/92	92/89	96/92	96/91	97/91	89/81
Modulus at 100% elongation:							
psi	3020	2560	2030	2435	2200	2460	1490
kg/cm	212	180	143	171	155	173	105
Elongation at break (%)	210	250	315	290	360	230	370
Tensile strength:							
psi	3360	3310	2865	3195	3060	3180	2800
kg/cm	236	233	201	225	215	224	197
Clash–Berg T_f (°C)	5	1	−1	−3	−3	1	−24
Percent weight loss:							
Air volatility, 16 h at 106 °C	2.7	1.0	0.6	0.9	0.4	0.5	6.0
Soapy water, 1 day at 98 °C	8.6	4.3	0.8	5.0	3.7	3.4	8.9
Mineral oil, 1 day at 49 °C	0.2	0.7	0.4	0.9	0.5	0.3	3.4
Hexane, 1 h at room temperature	0.5	0.6	0.3	0.3	0.3	0.2	15.0
Rub-off, 4 h at 50 °C	1.4	0.2	1.4	0.5	—	0.1	3.0

plasticizers (Admex® plasticizers) in 1995. Since then, Witco polymerics (Drapex® plasticizers) and Caschem polymerics (Uniflex® plasticizers) were also purchased by Velsicol Chemical and are now under the Admex trade name. C.P. Hall products are sold under the trade names of Paraplex® and Plasthall®. Cognis (Henkel) sells polymeric plasticizers under the trade name Edenol®.

8.4 CITRATE PLASTICIZERS

Citrates are versatile plasticizers for several applications. Citric acid is a naturally occurring tribasic acid that also carries a hydroxyl group, making it unique for plasticizer applications. This functionality makes the citrate family versatile. Citrates are used as plasticizers in the following applications:

- Acrylic resins
- Cellulosic polymers
- Vinyl acetate
- Nitrocellulose
- Vinyl chloride and vinyl chloride copolymers

TABLE 8.31 Performance of Low- to Medium-Molecular-Weight Polymeric Plasticizers

	Low-MW Admex	Medium-MW Admex			Control DOP	
	412	409	334F	429	67 phr	50 phr
Shore A hardness	72	75	76	74	70	82
Modulus at 100% elongation:						
psi	—	—	1400	—	990	1650
kg/cm	—	—	98	—	70	116
Elongation at break (%)	—	—	405	—	460	340
Tensile strength:						
psi	—	—	2600	—	2230	2980
kg/cm	—	—	183	—	157	209
Clash–Berg T_f (°C)	−30	−21	−22	−19	−39	−27
Percent weight loss:						
Air volatility, 16 h at 87 °C	1.8	0.9	0.8	0.8	7.0	6.8
Soapy water, 4 days at 50 °C	4.7	4.4	—	2.7	—	—
Hexane, 4 h at 25 °C	4.5	2.8	2.0	1.0	27	21
5% NaOH, 4 days at 25 °C	0.9	0.9	—	0.4	—	—
Migration resistance, % weight gain at 23 °C:						
Natural rubber	—	1.3	—	0.3	16.1	—
SBR	—	0.5	—	−0.2	12.9	—
Neoprene WRT	—	1.0	—	0.7	15.2	—
Butyl rubber 217	—	0.0	—	0.0	0.8	—
Hycar 1002	—	−1.3	—	0.6	4.2	—

TABLE 8.32 Formulation for Calendered Film for Electrical Applications

Raw Material	Parts by Weight (phr)
PVC resin, $K = 67$	100.0
Admex® 6996 or 312	55.0
Dibasic lead phthalate	5.0
Calcium stearate	1.0
Low-molecular-weight polyethylene wax	0.3
High-molecular-weight polyethylene wax	0.5
Antimony trioxide	3.0
Carbon black	1.0

TABLE 8.33 Test Results for Calendered Film for Electrical Applications

Property	Test Method	Result
Shore A hardness, 10 s	ASTM D-2240	82
Electrical properties:		
Dielectric strength	ASTM D-419	
Dry		1172 V/mil
Wet		1003 V/mil
Volume resistivity	ASTM D-257	1.37×10^{13} ohm cm
Surface resistivity	ASTM D-2305	3.00×10^{11} ohm
Dielectric constant, SIC	ASTM D-150	5.63
Dissipation factor	ASTM D-150	0.032
Brittle temperature	ASTM D-746	−18.5 °C
Oil extraction resistance, 24 h at 50 °C, 20 mil-thick sample	ASTM D-543	1.34% weight loss
Volatility resistance, 24 h at 90 °C, 20 mil-thick sample	ASTM D-1203	0.8087% weight loss
Dynamic mill stability	NTC 0057	
Time to degradation, 1 ft × 1 in sample sticks to roll		65 min

TABLE 8.34 Extrusion Test Formulation

Ingredient	Parts by Weight
PVC resin, $K = 67$	100
Admex® 6187	50.0
TOTM	15.0
Dibasic lead phthalate	10.0
Paraffin wax	0.5
Calcined clay	5.0
Bisphenol A	0.3

TABLE 8.35 Extrusion Application Test Results

Test	Test Method	Result
Shore A hardness, 10 s	ASTM 2240	89
Dielectric strength:	ASTM D-419	
Dry		1290 V/mil
Wet		1251 V/mil
Volume resistivity	ASTM D-257	7.74×10^{12} ohm cm
Surface resistivity	ASTM D-2305	3×10^{11} ohm
Dielectric constant	ASTM D-150	5.87
Dissipation factor	ASTM D-150	0.0396
Brittle temperature	ASTM D-746	−16 °C
Oil extraction resistance, 24 h at 50 °C	ASTM D-543	1.30% weight loss
Volatility, 24 h at 90 °C	ASTM D-1203	0.2422% weight loss

TABLE 8.36 Vinyl Foam Formulation

Ingredient	phr
PVC, dispersion-grade: Geon® 124A	51
PVC, suspension-grade: Geon® 217	49
Admex 523 plasticizer	100
Calcium carbonate	21.4
Azodicarbonamide	6.2
Akrostab® ABC-1	1.2
VS 103 foam stabilizer (air products)	2

TABLE 8.37 Decals and Foams (Plastisol and Organisol Applications) Formulation

Ingredient	Parts by Weight (phr)
PVC resin, dispersion-grade	70.0
PVC resin, blending-grade	30.0
Admex 770	50.0
Ba/Zn stabilizer	3.0
Ester plasticizer diluent	33.0
Aliphatic hydrocarbon diluent	7.0

TABLE 8.38 Decals and Foams (Plastisol and Organisol Applications) Test Results

Test	Test Method	Result
Shore A hardness, 10 s	ASTM D-2240	89
Surface energy:	ASTM D-2578	
1 hour		38 dyn/cm
24 hours		38 dyn/cm
1 week		37.5 dyn/cm
Viscosity at 25 °C:	ASTM D-4878	
1 hour		3036 Pa s
1 day		3620 Pa s
7 days		3675 Pa s
Gel temperature	NTC-0056	95 °C
Fusion temperature	NTC 0056	182 °C

There are numerous other applications for the salts and esters of citric acid besides those suggested by the polymers listed above, but the focus is vinyl. Table 8.45 lists the vinyl applications for select citrates.

Certain citrate esters are functioning plasticizers for vinyl applications, an important attribute being their FDA sanctions and their safety and environmental status as

TABLE 8.39 Formulations for Calendered Films for Packaging Decals and Related Applications

Ingredient	Parts by Weight (phr)
PVC resin, $K = 67$	100
Admex 6985	40.0
Ground $CaCO_3$	10.0
Ba/Zn stabilizer	4.0
Processing aid	1.0
Lubricating process aid	2.0
Oxidized polyethylene wax	0.25
TiO_2	12.0

TABLE 8.40 Test Results for Calendered Films for Packaging Decals and Related Applications

Test	Test Method	Result
Shore hardness, 10 s	ASTM D-2240	89
Volatility, 24 h at 90 °C, 20 mil sample	ASTM D-1203	0.7727% weight loss
Surface energy:	ASTM D-2578	
1 hour		38 dyn/cm
24 hours		37.5 dyn/cm
1 week		38.5 dyn/cm
Dynamic mill stability:	NTC 0057	
Time to degradation, 1 ft × 1 in sample sticks to roll		65 min

TABLE 8.41 Starting Formulation for Extraction-Resistant Upholstery Fabric—Automotive, Commercial Residential

Ingredient	phr
PVC ($K = 65$–72)	100
Polymeric/linear phthalate 3/1	70–80
ESO or tall oil fatty acid ester	3
Ba/Cd or Ba/Zn stabilizer	3
Lubricant	0.2
$CaCO_3$	10–25
Pigment	5–10

nontoxic additives. Whereas some plasticizers are being challenged by regulatory issues and unscientific protest, citrates can be used in sensitive applications such as in vinyl medical devices or children's toys (mouthables). Table 8.46 lists FDA sanctions that may be applicable to vinyl applications.

TABLE 8.42 Starting Formulation for Extraction-Resistant Baby Wear and Hospital Sheeting

Ingredient	phr
PVC ($K = 65-72$)	100
Plasticizer system	60–80
Epoxidized soybean oil	3
Stabilizer (low level)	3
Lubricant (if needed)	0.2
$CaCO_3$	0–10
Pigment	0–3

TABLE 8.43 Starting Point Formulation for Gasoline-Resistant Clothing, Tarpaulins, Hoses, and Sailor Products

Ingredient	phr
PVC ($K = 65-72$)	100
Medium- to high-molecular-weight polymeric	80–100
Epoxidized soybean oil	3
Stabilizer	3
Lubricant	0.2–0.5
Acrylic processing aid (e.g., Acryloid K-120ND	2
Pigment	0–5

TABLE 8.44 Starting Formulation for Oil-Resistant Shoe Soles

Ingredient	phr
PVC (usually injection-molding grade, $K = 65$)	100
Low- to medium-molecular-weight polymeric	39
DOA (low-temperature plasticizer)	31
Epoxidized soybean oil	10
Ba/Cd, Ba/Zn stabilizer	3
Lubricant	0.25
Pigment	0–5

8.4.1 Commercial Citrate Plasticizers

Not all the citrates are used in vinyl. The following are some of the products that are recommended for vinyl applications:

- Acetyl tri-n-butyl citrate (Citroflex A-4) is recommended for use in vinyl children's toys, food wraps, beverage tubing and helmet crown liners.
- Acetyl tri-n-hexyl citrate (Citroflex A-6) is recommended for medical devices.
- n-Butyl tri-n-hexyl citrate (Citroflex B-6) is also recommended for medical devices.

TABLE 8.45 Vinyl Applications for Citrates

	Plasticizer Type		
	A-4[a]	A-6[a]	B-6[a]
Medical Plastics			
Extracorporeal tubing	×	×	×
Blood bags		×	×
Intravenous solution containers and sets		×	×
Catheters		×	×
Food Contact Products			
Food wraps and films (PVC and PVDC)	×		
Beverage tubing	×		
Crown liners	×		
Food containers	×		
Tinplate lubricant	×		
Other Industrial Uses			
Children's toys	×		

[a] A-4 = acetylated tributyl citrate; A-6 = acetylated trihexyl citrate; B-6 = butylated trihexyl citrate.

TABLE 8.46 FDA Sanctions for Citrates

Product	21CFR Listing	Subject
Citroflex A-4, A-4 special	175.105	Component of adhesives
	175.300	Resinous and polymeric coatings
	175.320	Resinous and polymeric coatings for polyolefin films
	175.380	Xylene–formaldehyde resins condensed
	176.170	Components of paper and paperboard in contact with aqueous and fatty foods
	177.121	Closures with sealing gaskets for food containers
	178.391	Surface lubricants used in manufacture of metallic articles
	181.27	Prior sanctioned plasticizers
		Flavor Extracts Manufacturers Association (FEMA)
		EEC Directive 90/128 for food film, List 8
		EPA list of inert pesticide ingredients

8.4.2 Citrate Plasticizer Chemistry

Citric acid is a unique raw material for plasticizers. The process of manufacture of these products, while more complicated than with esters such as benzoates or phthalates, is, however, fairly straightforward. The preparation is as follows:

$$\text{citric acid} + \text{alcohol} \rightarrow \text{citrate partial ester} + \text{water} \tag{3}$$

$$\text{citrate partial ester} + \text{acid anhydride} \rightarrow \text{fully esterified citric acid} \tag{4}$$

Partial citrate esters (with free hydroxyl functionally available) are useful as plasticizers for different applications. As an example of a completely reacted plasticizer, for acetyl tri-n-butyl citrate, the reactions are as follows:

$$\text{citric acid} + 3\ \text{n-butanol} \rightarrow \text{tri-n-butyl citrate} + 3\ \text{water} \tag{5}$$

$$\text{tri-n-butyl citrate} + \text{acetic anhydride} \rightarrow \text{acetyl tri-n-butyl citrate} \tag{6}$$

The patent literature details techniques to manufacture citrates.[19–21]

8.4.3 Citrates in Vinyl

Table 8.47 lists a melt process formulation and Table 8.48 vinyl performance of select citrates in a melt processed generic composition that is compared with DEHP and DEHA.[19–23]

Acetyl tri-n-butyl citrate, which is recommended for toy applications, is:

- Less permanent than DEHP and DEHA, but
- Is similar in efficiency to DEHP

Plastisols are the compounds of choice for many toys (rotational molding), and acetyl tri-n-butyl citrate will yield plastisols with the required rheology. Table 8.49 lists a plastisol formulation and Figs. 8.10 and 8.11 illustrate the performance of a generic formulation plastisol with acetyl tri-n-butyl citrate. This citrate will yield readily processable plastisols.

The higher-molecular-weight citrates, acetyl tri-n-hexyl citrate and n-butyl tri-n-hexyl citrate, are recommended for medical devices such as blood bags and tubing. Patents for these applications list specific data on these applications.[19–21] The higher-molecular-weight citrates are more permanent but less efficient than DEHP.

TABLE 8.47 Base Formulation for Citrate Evaluation

Raw Material Type	Description	Parts by Weight
Resin	Suspension PVC, $K = 70$	100
Plasticizer	As listed in Table 8.48	50
Stabilizer	Ca/Zn type	2.5
Lubricant	Stearic acid	0.25

TABLE 8.48 Citrate Vinyl Performance in the Formulation of Table 8.47

	Plasticizer				
Characteristics	DEHP	DEHA	A-4	A-6	B-6
Hardness, shore A	79	78	78	81	81
Tensile strength (psi)	2748	1797	2862	2978	2924
Ultimate elongation (%)	395	414	400	390	427
100% modulus (%)	1368	1092	1348	1574	1362
T_4 (10,000 psi) (°C)	−8.4	−30.8	−7.6	−9.1	−11.9
T_f (100,000 psi) (°C)	−38.8	−66.5	−35.6	−41.6	−48.7
Brittle point (°C)	−24.5	−56.5	−18.5	−26	−33.5
Volatile loss, air (%)	4.8	7.1	12.1	2.6	1.7
Volatile loss, A/C (%)	3.4	7.6	7	1.7	1.4
Water extraction (%)	0.7	1.5	1.2	1.9	1.7
Soapy water extraction (%)	2.7	11	9.5	5.4	2.2
ASTM oil #3 extraction (%)	11.4	34.7	10.9	13.8	15.7
Silica gel migration (%)	12.2	23	17	4.4	3.6

TABLE 8.49 Plastisol Formula for Citrate Evaluation

Component	phr
Medium-molecular-weight dispersion-grade resin	100
Plasticizer	As specified
Epoxidized soybean oil	3
Stabilizer (Ca/Zn)	1.5
Phosphite chelator	0.5
$CaCO_3$	Where specified

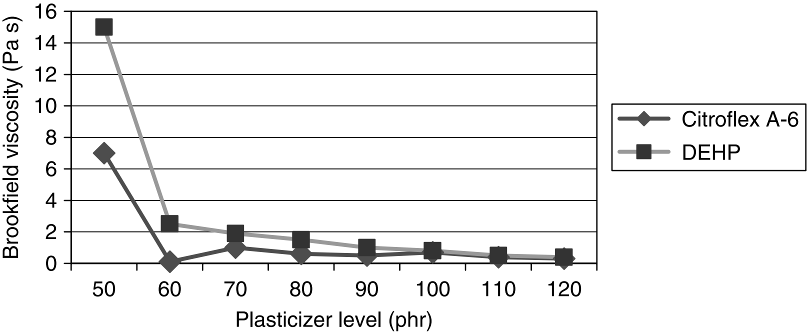

Figure 8.10 Brookfield RVT initial viscosity versus plasticizer level.

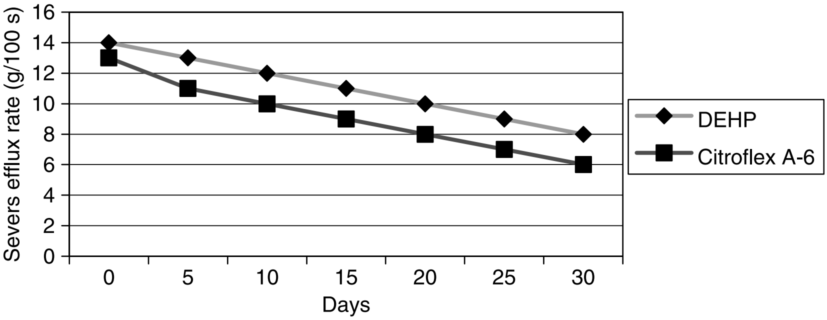

Figure 8.11 Severs efflux rate versus plastisol (57 phr plasticizer).

8.5 SUMMARY

Specialty plasticizers are used in vinyl compositions to provide performance that is beyond that which can be obtained with a general purpose phthalate. These plasticizers can be used by themselves in specific compositions, but are often used in combination with other plasticizers to complement each other's performance. Several major types of specialty plasticizers have been covered in this chapter: benzoate esters, polyester polymerics and citrate esters. Each class has specific performance attributes:

- *Benzoate esters*. As a class, these specialty plasticizers are known as high solvators for vinyl compositions. Within this class of plasticizers, the applications range from viscosity reducers for plastisols to bleed-resistant plastisols for screen ink. They are considered as phthalate alternates for applications requiring phthalate-free compositions.
- *Polyester polymeric plasticizers*. Polyester plasticizers are used because they are permanent. They range in average molecular weight from less than 1000 to greater than 13,000. Polymeric plasticizers are used in applications such as decals, gaskets, vinyl films, hoses, and the like, where extraordinary performance properties are required.
- *Citrates*. Citrate esters can be used in application areas that require regulatory sanctions, such as medical devices. Their safety profile and FDA sanctions, plus good performance in flexible applications, recommends their use in sensitive applications.

8.6 ACKNOWLEDGMENTS

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CHAPTER 9

Formulating Vinyl for Flame Resistance

PAUL Y. MOY

Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

9.1 BACKGROUND

Each year, fire and related events cause thousands of deaths that might otherwise have been saved if appropriate fire safety systems were in place. Given the extensive use of combustible materials in everyday lives, the question is not whether a fire will occur, but when and how prepared you will be. Will you know what to do in these situations, and how much time will you have to escape? Flame-retardant (FR) additives can help to an extent. Although these additives will not stop a fully evolved fire, flame-retardants can stall or impede the initiation and propagation of new fires and allow more time to escape. Luckily, in many cases, this is enough to avoid the loss of life and to minimize property damage.

Pure PVC is relatively nonflammable and has in fact been used in a number of applications as the FR component in thermoplastic composites. However, in flexible compounds, the plasticizer converts vinyl into a fire hazard. Non-FR plasticizers such as phthalates and adipates can contribute greatly to the flammability of a composite, as they can be 30 percent or more of its ingredients. Substituting these plasticizers with less flammable types can alter the combustion behavior. There are many different ways of flame-retarding flexible vinyl; a typical approach is to use an organophosphate as a partial or full substitution of the plasticizer component. However, because of the relative costs of phosphate esters, most users will formulate to the minimum levels necessary to pass FR requirements.

9.1.1 History

Although many might argue the origins of today's flexible vinyls, most would agree that the 1920–1930s were a significant period. Work in that era found researchers looking for alternatives to natural rubber products, which at that time were sourced from costly, faraway regions of the world. In one such project, Waldo Semon, a chemist at the B.F. Goodrich Company, tried to use synthetically produced PVC materials to replace the natural rubber products employed in the interior lining of tank cars for corrosion resistance.[1] Using vinyl resin and *o*-nitrodiphenyl ether, he serendipitously discovered that this mixture, unlike other artificial rubber composites, produced a rubbery gel that could be bounced like a ball. Further experiments with other solvents and organic compounds produced flexible vinyls that could be used to treat fabrics and other materials for waterproofing, solvent, and chemical resistance, significantly better than the natural rubbers used previously. The flexible vinyl composite resin afforded a cheap and effective alternative to natural elastomers.

One of the first plasticizers used commercially for flexible vinyl was tricresyl phosphate (TCP). It was recognized as having flame-resistant characteristics in addition to being an excellent plasticizer for vinyl. General Electric was one of the first companies to market resin blends of PVC/TCP plasticizer as a family of FR composites called Flamenol®.[2] Through the versatility of PVC and its additives, a number of varied applications have evolved.

The modern use of FR vinyls is pervasive throughout our society. One of the largest markets for flexible vinyls is in insulation and jacketing applications for wire and cable products. This market is segmented into a number of groups requiring different levels of flame resistance. For the FR PVC plenum market (wiring for data/communication applications allowed inside air conduits of high-rise buildings), the market is perceived to be in excess of 50 million pounds per year. This application requires a premium grade of vinyl composite, as it must pass rigorous flammability and smoke requirements. Some of the challenges facing this vinyl market today are from nonhalogen polyurethanes and FEP (fluorinated olefin) products.

9.2 PHOSPHATE ESTERS

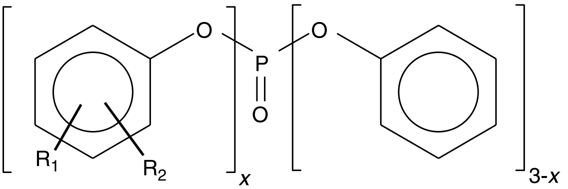
Of this family of products, triaryl phosphates (TAP) and alkyl diaryl phosphates (ADP) are the two important categories of FR plasticizers for PVC. Trialkyl phosphates are considered too volatile for most vinyl processes, and are more commonly found in other applications, such as leveling agents or antifoam additives. In vinyl, TAP and ADP plasticizers are used to flame-retard thin films and laminates for articles such as wall covering, tarpaulins (transportation), and vinyl-coated furniture fabric. Another major application area is in vinyl for electrical insulation in wire and cable. In addition to these applications, phosphate esters are used as functional fluids for hydraulic equipment (metal industries, power generation, and aircraft hydraulic systems) and as additives in formulated lubricant systems. As flexible vinyl composites are usually defined by their additives, when formulated correctly, phosphate esters can help produce a very cost-efficient vinyl composite capable of very low smoke and flammability. In nearly all markets, phosphate esters are valued primarily for their FR properties, and the distinction from function and plasticization is sometimes obscured.

9.2.1 Cresylic Phosphates

As one of the first plasticizers used on a commercial scale, TCP was originally produced using natural feedstock; that is, petroleum-derived (mixtures of *ortho*, *meta*, and *para*) cresols. With the success of TCP, variations of this phosphate ester became popular. Cresyl diphenyl phosphate (CDP) and trixylenyl phosphate (TXP) each in their own right were found to be useful and offered distinct characteristics such as low volatility and good temperature stability (Fig. 9.1).

Unfortunately, cresylics fell out of favor because the *o*-cresyl phosphates were found to be strong neurotoxins.[3] The manufacture of these plasticizers (using only the *m*- and *p*-cresol isomers) became more costly and compounders turned to other cheaper plasticizers.

Today, TCP made from *o*-cresol-free feedstock is still used in vinyl composites for clear agricultural film applications (greenhouses) in Asia. Cresyl diphenyl phosphate is widely used in Europe and Asia because of its high efficiency and very low cost. For most U.S. vinyl markets, however, it is not considered, because of lingering toxicity concerns. However, modern cresyl phosphates, largely free of the *o*-cresyl isomer, are not serious neurotoxins, and are seen in applications as flame-retarded, low-foaming hydraulic fluids in power generating stations.



$x = 0, \ldots, 3$
$R_1 = R_2 = H$: TPP
R_1 = methyl, $R_2 = H$: TCP ($x = 3$), CDP($x = 1$)
$R_1 = R_2$ = methyl: TXP ($x = 3$)
R_1 = isopropyl, $R_2 = H$: IPP ($x = 1$)
R_1 = t-butyl, $R_2 = H$: TBPP ($x = 1$)

Figure 9.1 Triaryl phosphates from synthetic alkylphenols.

TXP has been used where high-temperature performance and/or long-term heat resistance are important. One of its early uses was as a flame-resistant hydraulic fluid for steel manufacturing, where high ignition temperatures were important. Because of its low volatility and antifogging characteristics, TXP also found uses in agricultural (greenhouse) film or automobile vinyl seating. Today, TXP is more typically seen as a functional fluid for electrohydraulic systems in power generation units, and its use in PVC has been greatly reduced over the years.

Triphenyl phosphate (a low-melting solid, about 50 °C), although a component of many phosphate ester plasticizers, is not typically used in flexible PVC because of its marginal compatibility. It is more commonly seen as a flame-retardant for engineering resins or a processing aid for photographic film.

9.2.2 Isopropylphenyl Diphenyl Phosphate

Variations on TCP have evolved, substituting the cresol (which has become more costly) with a synthetic isopropylphenol–phenol mixture to produce a mixed phosphate ester, often denoted as isopropylphenyl diphenyl phosphate (IPP) (Fig. 9.1). This development was originally forced by the erratic supply and pricing of *ortho*-isomer-free cresols. The IPPs are made with varying mixtures of isopropylphenol and phenol moieties and phosphorus oxychloride. These variations have been effectively substituted for the various cresylic phosphates. For example, an IPP prepared with roughly 60 percent isopropylated phenol could be substituted in vinyl for TCP; an IPP phosphate with roughly 50 percent alkylphenol substitution can replace CDP. A 90 percent plus analog would mimic properties of TXP in flexible PVC. The majority of these products are supplied by three companies: Albemarle (Antiblaze®), Chemtura (formerly Great Lakes Chemicals—Reofos®/Kronitex®), and Supresta (Phosflex®).

Dr Joseph Green, formerly with FMC, points out that the isopropylated triphenyl phosphates are distinct compared with TCPs in that they have high plastisol fusion rates but small increases in viscosity during storage.[4] In treating fabrics, this property is advantageous in allowing more time for effective coating and penetration.

9.2.3 t-Butylphenyl Diphenyl Phosphate

A related product is t-butylphenyl diphenyl phosphate (TBPP) (Fig. 9.1), made from t-butylphenols and phosphorus oxychloride. Similar to the isopropylphenol analogs, these reactions produce a mixed t-butylaryl phosphate ester product. TBPP was originally introduced in the 1970–1980s as a fluid for hydraulic applications, but this compound has also found a useful niche in engineering resins and flexible PVC. It is available from Supresta as Phosflex® 71B and from Great Lakes Chemicals as Reofos® 100B. By itself, it has inferior plasticizing activity compared with the IPP and cresylic plasticizers, but when blended with a more efficient plasticizer, its activity is usually adequate for many flexible vinyl compounds. TBPP also has some advantages of thermo-oxidative stability. By most standards, it has excellent FR activity and imparts rapid gelation characteristics to PVC plastisol formulations, as well as good resistance to microbial damage.

Of the TAPs, the following groups allow for varying degrees of plasticity (cresylics > isopropylated > butylated):

- Cresylics (cresyl diphenyl and tricresyl phosphates)
- Isopropylated TAPs (various degrees of substitution)
- *t*-Butylated TAPs (various degrees of substitution)

As a class, the TAPs are typically better flame retardants than other phosphate esters, but may produce higher levels of smoke during combustion (Table 9.1) than are produced by nonphosphate plasticizers. Incorporating low-smoke additives

TABLE 9.1 Cone Calorimeter (Flux 50 kW/m^2): Triaryl Phosphates in S-PVC Resin

Material(s)[a]	Level (phr)	Time to Ignition (s)	Time to Flame-Out (s)	Peak Heat Release Rate (kW/m^2)	Effective Heat of Combustion (MJ/kg)	Total Heat (kJ)	Average Smoke (m^2/kg)
DIDP (control)	—	16	210	391 (at 50 s)	17.2	86	5.5
Sb_2O_3 (DIDP)	6	18	202	374 (at 90 s)	17.1	84	5.2
Phosflex 31L (IPP)	—	20	244	265 (at 56 s)	14.6	76	5.1
Phosflex 71B (TBPP)	—	20	250	277 (at 44 s)	16.9	83	5.3
Lindol (TCP)	—	22	244	297 (at 58 s)	14.5	84	5.4

[a] DIDP = diisodecyl phthalate; IPP = isopropylphenyl diphenyl phosphate; TBP = t-butylphenyl diphenylphosphate; TCP = tricresyl phosphate.

TABLE 9.2 Phosphate Ester Plasticizers in PVC

Phosphate Ester Type	Viscosity at 25 °C (mm/s)	Density at 25 °C	Shore A Hardness	Cold Flex Clash–Berg T_f (°C)	Oxygen Index (% O_2)
Isopropyl phenyl diphenyl	44.5	1.183	74	−2	32.6
Isopropyl phenyl diphenyl	48	1.174	75	−2	32.5
Isopropyl phenyl diphenyl	57	1.164	76	−1	32.5
Isopropyl phenyl diphenyl	93	1.136	78	+1	32
Cresyl diphenyl	36	1.202	73	−4	33
Tricresyl	60	1.158	74	0	32.5
Trixylenyl	95	1.134	76	+4	32
t-Butylphenyl diphenyl	81	1.165	89	+11	32
2-Ethylhexyl diphenyl	16	1.087	70	−24	28.6
Isodecyl diphenyl	22	1.065	71	−20	28.1
		For Comparison			
Dioctyl phthalate	56	0.980	71	−24	24
Diisononyl phthalate	85	0.970	75	−19	24
Tetrabromophthalate	1036	1.54	94	+18	37.5

can complement these systems if needed. In general, TAPs are less volatile and have higher thermal stability than ADPs; however, as a group, triaryl phosphates are not efficient plasticizers compared with other phosphate esters.

9.3 COMPARISON OF FR AND NON-FR PLASTICIZERS

Comparative data in Table 9.2 was selected from a Great Lakes Chemical bulletin “Specialty Plasticizers for PVC” for a formulation containing 100 parts PVC suspension polymer, 60 parts per 100 of resin (phr) of the indicated plasticizer, 1 phr Irgastab 17M and 0.2 phr Irgawax 0.2.[5]

9.4 COMPARISON OF COMBINATIONS OF PLASTICIZERS AND OTHER ADDITIVES

Some more or less advantageous combinations (according to differing criteria) are shown in Table 9.3. The TAP used in this example is an IPP in a suspension PVC formulation.[6] The data were obtained in the cone calorimeter at a heat flux of 50 kW/m^2.

TABLE 9.3 Triaryl Phosphates with Other FR Additives

Additive(s) to PVC	Additive Level (phr)	Burning Time (s) in Cone Test	Peak Heat Release Rate (kW/m^2)	Time to Peak Heat Release (s)	Char (wt. %)	LOI (% O_2)
DIDP	50	128	45.1	35	6	23.5
Antimony oxide (AO)	6	134	36.8	48	12	29.8
AO/Zn-borate (ZB)	6/6	144	42.1	38	22.4	30.5
Triaryl phosphate (TAP)	50	148	40.8	46	7.7	31.8
TAP/ZB	50/6	200	30.6	54	10.8	34.7
TAP/AO	50/6	180	44.4	70	9.2	32.9
TAP/AO/ZB	50/6/6	176	23.9	34	18.3	33.3
TAP/AO/ZB/ATH	50/6/6/30	300	25.4	52	10.5	37.1

These data show that the preferred formulation may depend on the criteria used. Some advantage is seen on cone calorimetry in combining antimony oxide and zinc borate. The combination of the TAP with antimony oxide, while not actually antagonistic, shows a distinctly less-than-additive effect and is thus relatively inefficient. In terms of the limiting oxygen index (LOI), zinc borate appears superior to antimony oxide in combination with the TAP. The presence of ATH produces a possibly useful slow-burning effect.

9.4.1 Alkyl Diphenyl Phosphates

The second class of FR phosphate esters used in flexible vinyls is the alkyl diaryl phosphates (ADP) (Fig. 9.2 and Tables 9.4 and 9.5). The most common approach for manufacturing these materials is by reaction of phosphorus oxychloride with the sodium salt of the alcohol. There are three major types, differing in the alkyl group: reaction products of isodecyl alcohol, 2-ethylhexanol or linear C_{12}–C_{14} alcohols. The advantages of these products are their low-temperature flexibility and/or lower volatility with the longer-chain alkyl group.

Besides being excellent plasticizers, one of the most significant traits of ADPs is low smoke generation, especially for vinyl wire and cable. As the use of electronics grows in everyday life, more and more data and communication cabling for computer networking and phones is routed through existing conduits such as HVAC ductwork. There can be miles of cables strung throughout these ducts, especially in high-rise buildings. When the cabling is upgraded, typically new wire is installed over the

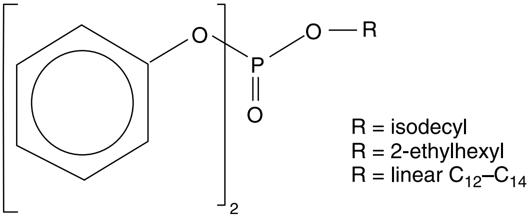


Figure 9.2 Alkyl diphenyl phosphate.

old wires; the outdated cables are not removed. These outdated wires remain behind as a potential smoke and fire hazard, and must be formulated to contribute minimally to a fire scenario.

9.4.2 2-Ethylhexyl Diphenyl Phosphate

The 2-ethylhexyl analog (EHDP) has the advantage of FDA clearance for certain food-grade coatings used for packaging applications. It is also claimed to improve UV stability and resistance to bacteria in vinyl articles when used in mixtures (10–15 percent by weight) with phthalate plasticizers. Although slightly more volatile than the other alkyl diphenyls, this highly efficient plasticizer is an excellent choice for flame-retarding vinyls and vinyl alloys (PVC/nitrile rubber), especially in low smoke applications. The key manufacturers of this product are Ferro (Santicizer® 141), Supresta (Phosflex® 362), and Lanxess (Disflamoll® TPO).

9.4.3 Isodecyl Diphenyl Phosphate

Isodecyl diphenyl phosphate (IDDP) is also an excellent choice for flame-retarding PVC products. This phosphate is slightly less volatile than the 2-ethylhexyl version and also has excellent plasticizing efficiency. IDDP finds use in a number of sheet good applications and PVC/nitrile rubber alloy types (insulative wrap for conduit), where there is a premium on low smoke and good low-temperature flexibility. This product is produced by Ferro (Santicizer® 148) and Supresta (Phosflex® 390).

TABLE 9.4 LOI of Alkyl Diaryl Phosphates Versus Triaryl Phosphates

Phosphate Ester Type	LOI (%O_2)
2-Ethylhexyl diphenyl phosphate	28.1
Isodecyl diphenyl phosphate	27.8
t-Butylphenyl diphenyl phosphate	31.2
Triphenyl phosphate	31.5
Isopropylphenyl diphenyl phosphate	31.8

PVC 100 parts, plasticizer 50 parts, stabilizers 5 parts.

TABLE 9.5 Thermogravimetric/DSC Testing of Phosphate Esters

Phosphate Plasticizer Type	DSC[a] Onset Decomposition Temperature (°C)	TGA-Isotherm 225 °C 5% Weight Loss (min)	 10% Weight Loss (min)
Isodecyl diphenyl phosphate	175	6.6	8.8
Linear alkyl $C_{12}-C_{14}$ diphenyl phosphate	182	10.2	16.2
Isopropylphenyl diphenyl phosphate	214	7.2	10

[a] 10 °C/min ramp.

9.4.4 Linear Alkyl Diphenyl Phosphates

The linear $C_{12}-C_{16}$ ADP ester is used primarily for wire and cable applications and has some performance advantages preferred over the other ADPs. It has lower volatility, slightly better low-temperature flexibility, and excellent low-smoke characteristics in vinyl formulations. However, it is typically more expensive than the other ADPs, and can usually be found in premium wire (plenum-grade) applications. This phosphate ester is manufactured by Ferro (Santicizer® 2148) and Unitex (Uniplex® FRX 47-88).

As a class, ADP plasticizers afford reasonable FR efficiency with exceptionally low smoke characteristics, but typically at a higher cost than most triaryl phosphates.

9.5 FR AND FLAME PROPAGATION MECHANISMS

To understand the approaches for solving flammability and smoke issues, one must understand how a fire propagates. Fortunately, there are usually several pathways to achieve the desired fire ratings, and the reasons for and against each system will be discussed.[7,8] The simplest way to show this is in the triangle of flame propagation (Fig. 9.3). All three aspects of this triangle must be present in the correct proportions

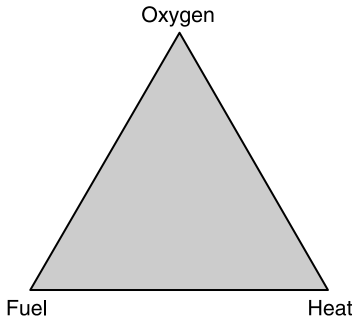


Figure 9.3 Flame propagation triangle.

to sustain optimal flame propagation. Should any of the three variables change, the growth of the fire can be upset to the point of extinguishment. As a practical example, in the home, the fuel source might be the foam cushion of an upholstered chair and the ignition source a lit cigarette (under normal conditions, atmospheric oxygen is always present at 21 percent). If the cigarette has sufficient contact with the cushion, it can ignite and grow in flame size to involve other articles in the room. Once critical conditions are met, "flashover" can occur where the temperature of the fire has grown sufficiently to ignite all the combustibles in a given area. Eventually, everything in the room will be consumed by the intense heat, which will probably spread to the rest of the house. If any element(s) of the triangle is changed, the intensity and growth potential of the fire will be similarly affected.

9.5.1 FR Mechanisms

FR mechanisms affecting these characteristics come in all sorts of shapes and sizes, but the following are some of the most common pathways.

Vapor Phase Vapor phase-active flame retardant(s) are those that decompose into free-radical scavengers, rendering combustible gases less flammable. This is the typical mechanism for halogenated composites, where either hydrogen bromide or antimony trihalide (from the halogenated component plus antimony oxide) intercepts the most reactive species (generally OH radicals, H atoms, or atomic oxygen), which are key species in the branching steps of the flame chemistry. Other halogen sources such as iodine and fluorine are not as effective, because they are either too unstable or costly (iodine) or bound too tightly (fluorine) to be used as vapor-phase flame retardants. The physical action of halogen flame retardants (by acting as heat sinks) of the halogen species also plays a significant part in their vapor-phase flame retardant action.

Solid (Condensed) Phase Solid phase fire retardant(s) alter the physical burning characteristics by either forming an insulative fire barrier or by changing the surface morphology to interfere with the release or generation of combustible gases. This mechanism is commonly seen with phosphorus-based flame retardants.

Endothermic Endothermic additives can sublime or absorb heat in their decomposition, evolving inert gases (usually water) to dilute the fuel and/or lower the temperature of the flame front. Hydrated mineral fillers such as alumina trihydrate (aluminum trihydrate, ATH) or magnesium hydroxide ($Mg(OH)_2$) and melamine or its salts (phosphates, cyanurates, etc.) are examples of this methodology. Use of ATH is discussed in Section 16.3 and magnesium compounds in Section 16.4.

More often than not, fire-retardant systems use combinations of these pathways as having the best potential for reducing the chances for fire growth.

Characteristics of effective flame retardants are:

- Additive decomposes near (preferably slightly below) the degradation temperature of the host resin
- Minimal effect on composite properties
- Compatible with host polymer

- Low toxicity
- Recyclable
- Low volatility
- High thermal stability

Other properties include:

- High hydrolytic stability
- Good weatherability
- Low-temperature composite ductility
- Low cost

9.6 FR SYNERGISTS

Although phosphate esters replace a portion of the flammable plasticizer in flexible PVC composites, these systems can be further enhanced with other options. Quite often, more than one mechanistic approach or blend of additives is the most cost-effective route.

9.6.1 Zinc Derivatives

Another common FR additive for PVC formulations is zinc borate (ZB). This product is suggested as a partial replacement for antimony oxide and also functions as a smoke suppressant for vinyl composites (Fig. 9.4).[9] ZB additionally can suppress glowing embers because it alters the surface morphology (char former) of the affected area. Use of ZB and related products, such as zinc hydroxystannate, is discussed in Section 16.5.

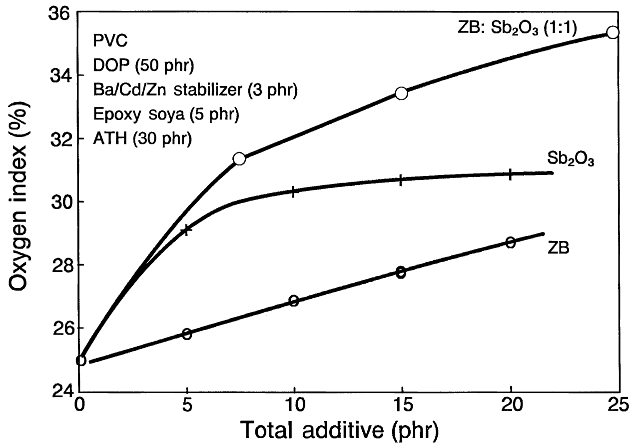


Figure 9.4 Oxygen index of flexible PVC formulations.

TABLE 9.6 Properties of FR-PVC using BrDOP[13]

	Formulation[a]				
Plasticizer(s) (parts):	1	2	3	4	5
BrDOP	—	20	40	60	93.4
TOTM	60	47.2	34.3	21.5	0
Tensile modulus (psi)	1640	1740	1760	1830	1980
Tensile strength (at break) (psi)	1860	1880	2050	2320	2520
Tensile elongation (%)	308	286	278	263	239
Low-temperature brittleness (°C)	−22	−20	−14	−14	−6
Shore A	88	88	88	90	92
LOI (%O_2)	27	31	33	36	42
NBS smoke					
Smoldering (Dmc)	200	190	180	170	140
Flaming (Dmc)	450	450	440	180	170

[a] PVC (Geon 30), 100 parts; BrDOP, varied (formulation held in constant volume: 61 ml); TOTM, varied (formulation held in constant volume: 61 ml); lead stabilizer, 5 parts; antimony oxide, 15 parts.

TABLE 9.7 Effect of Inorganic Additives: Oxygen Index (%O_2)[15]

	Inorganic Additive				
		$CaCO_3$	ATH	$MgCO_3$	$MgCO_3/Sb_2O_3$
Phosphate Plasticizer (50 phr)	None	20 phr	20 phr	20 phr	20/4 phr
Alkyl diphenyl	27.8	27.4	30.2	27.6	29.4
Triaryl (t-butyl)	31.2	30.7	32.9	32.4	33.7
Triaryl (isopropyl)	31.8	30.2	33.8	33.1	34

Test formulation: PVC, 100 parts; plasticizer, 50 parts; stabilizer, 5 parts; inorganic as shown.

9.6.2 Molybdenum Additives

Molybdenum compounds are regarded as the standard for low-smoke formulations, especially ammonium octamolybdates (AOM) for vinyl applications. Many studies claim that molybdates work in the solid phase, as most of the molybdenum is found in the char residue. Molybdates are said to reduce smoke by catalyzing the formation of *trans* polymer fragments so that it cannot form aromatic species, characteristic of soot. One producer uses an inert filler (talc) as the core support media onto which a zinc molybdate layer is precipitated on the surface. This coated core structure effectively provides smoke suppression at a lower manufacturing cost than neat molybdates.[10]

Physical mixtures of molybdenum trioxide with other metal oxides (copper, iron, and tin) are also reported to provide low-smoke characteristics.[11] However, flammability may increase due to the enhanced combustibility of these materials.

In contrast, tin and iron work partially like antimony trioxide as FR synergists. They have been suggested for use in vinyl and also nylon and other thermoplastic applications.[12] Formulating with molybdenum compounds is discussed further in Section 16.6.

There are a number of products that can be suitable as low-smoke additives and/or partial replacements for antimony oxide. Care must be taken with these zinc-based materials, as they can destabilize PVC if not properly formulated. Use of antimony oxide and related additives in vinyl is discussed in Section 16.2.

9.7 HALOGENATED PHTHALATE ESTERS

Another source of flame retardancy for flexible vinyls can be found in dioctyl tetrabromophthalate (BrDOP). BrDOP imparts excellent flame retardancy with relatively low smoke production. Also its structure is reported to be very stable (5 percent weight loss at 290 °C), well beyond the processing range of most vinyl compounds) with low volatility (Table 9.6).[13] BrDOP is used for plenum grade vinyls and other high-end FR-PVC applications. One manufacturer claims that mixed halogen (bromine and chlorine) phthalate esters have improved mechanical properties in addition to excellent FR properties (Table 9.6).[13]

9.8 CHLORINATED PARAFFIN

Various grades of chlorinated paraffin are used both as secondary plasticizers and as additional FR sources for halogens. These low-cost FR additives are claimed to contribute minimally to smoke generation while providing more chlorine for improved combustion resistance. Although chlorinated paraffins are used successfully in a number of thermoplastic applications, they have the potential to either destabilize (discolor) vinyl composites or leach to the surface (limited compatibility) if not properly formulated with other components.

More recently, Dover Chemicals (Chlorez®) claims a class of more efficient chlorinated paraffins that can reduce formulation costs by lessening the need for other FRs such as antimony oxide and phosphate plasticizers. This efficiency is realized by better manufacturing techniques (low branching), feedstock, and selecting optimal chain length for the paraffin.[14]

9.9 OTHER “NON-FR” PLASTICIZERS

Although not usually considered as a fire-retardant option for flexible vinyl, several “non-FR” choices can be made. While neat rigid PVC is relatively inflammable, plasticized flexible composites can be highly flammable. In flexible vinyl compounds, the greatest source of fuel will come from the plasticizer, and, although many systems are partially substituted with a FR plasticizer, the fuel value of these products can be the most significant property to consider. When maximum flame resistance is required and additional flexibility is needed, non-FR plasticizers such as polymerics and/or copolymer systems (low fuel value) can contribute to the composite's ductility while contributing minimally to its flammability. These alternatives can alter the combustion mechanisms discussed previously by contributing less fuel value than other plasticizers.

9.10 APPLICATIONS

How do all these additives help in passing FR standards? Most times, more than one additive is necessary to reach FR requirements, and they must work in harmony with other additives in matching or exceeding the required properties for a given application. Properties such as thermal stability, color (or absence of color), low-temperature ductility, and weatherability are a few notable characteristics important to the success of an application. All these things must be considered while keeping the formulation cost-competitive.

For calendered vinyls, there are a number of approaches to a successful FR formulation. In thin-film laminates, antimony oxide in combination with other inorganics can be successfully formulated to give a certain level of FR performance suitable for today's standards. A full or partial substitution of the base plasticizer with a phosphate ester can also be beneficial. Whereas smoke remediation is needed, adding one of the molybdates or zinc-based synergists and/or substituting the plasticizer with an alkyl diphenyl phosphate plasticizer can also be beneficial. Hydrated inorganic additives (ATH and/or $Mg(OH)_2$) can help reduce smoke formation by diluting the heavy soot /smoke with water vapor from released molecules of water. Sometimes, reinforced fabrics further complicate the systems because the fibers acts as a candle-like wick, impeding melt flow and behaving as a site for sustained burning. For applications that require higher standards for low smoke generation and flammability, more aggressive options will be needed.

Some examples of additive interactions are given in Table 9.7.[15] In this study, the vinyl formulations are varied by not only the inorganic but also the type of phosphate ester plasticizer used. The influence of these interactions is shown by the varying flame resistance (as judged by LOI) of the compounds.

9.11 FLAME SPREAD

While minimization of peak heat release is considered by most experts the single most important goal, it is also desirable to extend the time necessary to reach this point; that is, to suppress the rate of flame spread or growth. Several additives were studied in a suspension PVC resin to show the effects of combinations (Fig. 9.5).

In the same phosphate ester-plasticized composite (TAP, 50 phr), zinc borate, antimony oxide, and ATH were examined in the cone calorimeter (Stanton–Redcroft) at a radiant heat flux of 50 kW/m^2. Also included was a series of compounds plasticized

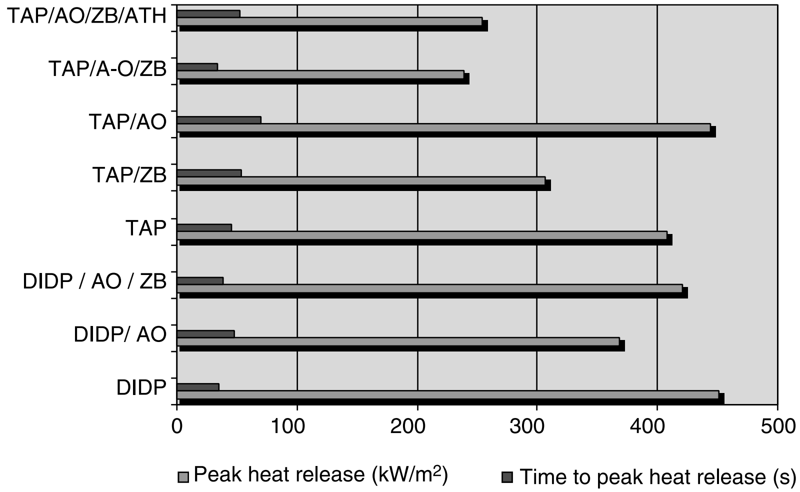


Figure 9.5 Effects of FRs on time to maximum heat release. (PVC, 100 parts; plasticizer, 50 parts; stabilizer, 5 parts; additives as shown).

by a phthalate ester (DIDP, 50 phr). It was found (as expected) that the most intense flame (highest peak heat release rate, PHRR) was seen with the phthalate ester compound. (Data presented in Fig. 9.5 also supports the previous claim of lost flame resistance, whereas the phosphate ester plasticizer/antimony oxide combination (TAP/AO) resulted in one of the highest heat release rates of the set.) Composites containing mixtures of all three additives (AO/ZB/ATH) with the phosphate plasticizer proved to be the slowest to reach its maximum heat (and also generated the lowest heat release). Similarly, this was one of the most difficult compounds to ignite (as judged by LOI: Table 9.8).

TABLE 9.8 Combination of FRs in PVC Composites

Material(s)	Additive Levels (phr)	LOI, 100 mil (%O_2)
	Phthalate Ester-Plasticized Composites	
DIDP	50	23.5
DIDP/antimony oxide	6	29.8
DIDP/AO/ZB	6/6	30.5
	Phosphate Ester-Plasticized Composites	
Triaryl phosphate ester (TAP)	50	31.8
TAP/ZB	50/6	34.7
TAP/AO	50/6	32.9
TAP/A-O/ZB	50/6/6	33.3
TAP/AO/ZB/ATH	50/6/6/30	37.1

PVC, 100 parts; plasticizer, 50 parts; stabilizer, 5 parts additives as shown.

TABLE 9.9 Wire and Cable Formulation

	Parts
PVC (Geon 30)	100
BrDOP	20
$C_{12}-C_{14}$ alkyl diphenyl phosphate	20
Polymeric plasticizer	10
ATH	60
Zinc molybdate	10
Ammonium octamolybdate (AOM)	20
Epoxidized soybean oil	3
Tribasic lead sulfate	5
Stearic acid	0.5

The formulations shown in Tables 9.9–9.11 are suggested as starting-point recipes for the stated applications.

Phosphate esters have proven their worth in a number of applications for vinyl. Having established themselves from the very beginning as practical solutions for flexible PVC, phosphate ester plasticizers have demonstrated a long history as efficient plasticizers and also as one of the major choices for resolving flammability issues.

TABLE 9.10 Auto Upholstery (FMVSS-302)[10]

	Parts
PVC	100
DIDP	70–80
$CaCO_3$	25–50
Epoxidized soybean oil	5
Stabilizer	3
Sb_2O_3	1.5–2.0
Zinc borate	1.5–2.0

TABLE 9.11 Wallcovering

	Parts
PVC	100
DIDP	26
Alkyl diphenyl phosphate ester	20
Sb_2O_3	2–4
Zinc borate	5–10
ATH	10–15
$CaCO_3$	40
Stearic acid	0.3
Stabilizer	3–5

TABLE 9.12 Suppliers

Manufacturer	Trade Name	Description
Albemarle	Antiblaze 519	Isopropylphenyl diphenyl phosphate
	Antiblaze 521	Isopropylphenyl diphenyl phosphate
	Antiblaze 524	Isopropylphenyl diphenyl phosphate
Dover Chemicals	Chlorez	Chlorinated paraffins
Ferro	Santicizer 141	2-Ethylhexyl diphenyl phosphate
	Santicizer 143	Proprietary blend of phosphate esters
	Santicizer 148	Isodecyl diphenyl phosphate
	Santicizer 154	t-Butylphenyl diphenyl phosphate
	Santicizer 2148	Proprietary alkyl diphenyl phosphate
	Santicizer 2248	Proprietary alkyl diphenyl phosphate
Great Lakes Chemicals	DP-45	Brominated phthalate ester
	Reofos 35	Isopropylphenyl diphenyl phosphate
	Reofos 50	Isopropylphenyl diphenyl phosphate
	Reofos 65	Isopropylphenyl diphenyl phosphate
	Reofos 95	Isopropylphenyl diphenyl phosphate
	Reofos 100B	t-Butylphenyl diphenyl phosphates
Supresta[a]	Phosflex 21L	Isopropylphenyl diphenyl phosphate
	Phosflex 31L	Isopropylphenyl diphenyl phosphate
	Phosflex 41L	Isopropylphenyl diphenyl phosphate
	Phosflex 71B	t-Butylphenyl diphenyl phosphate
	Phosflex 362	2-Ethylhexyl diphenyl phosphate
	Phosflex 390	Isodecyl diphenyl phosphate
	Phosflex 314	Proprietary blend
	Phosflex 321	Proprietary blend
Unitex Chemicals	Uniplex/FRX 47-88	Proprietary alkyl (C_{12}–C_{16}) diphenyl phosphate
	Uniplex FRP-45	Di-2-ethylhexyl tetrabromophthalate
	Uniplex FRP-44-57	Brominated/chlorinated phthalate ester

[a] Previously the Phosphorus Chemicals business unit of Akzo Nobel.

9.12 SUPPLIERS

In the United States, FR plasticizers are produced by the manufacturers listed in Table 9.12.

9.13 ACKNOWLEDGMENTS

I would like to thank Supresta U.S. LLC for their support and my fellow colleagues in the industry who willingly shared information presented in this chapter.

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CHAPTER 10

Impact Modification

MARK T. BERARD and C. MICHAEL VANEK

10.1 INTRODUCTION

An impact modifier is a material added in small amounts to a PVC compound to improve impact resistance. The impact modifier facilitates the redistribution of impact energy throughout the PVC matrix. It is mainly the PVC itself that absorbs the energy of the impact, and not the impact modifier. This chapter will review PVC impact theory, current PVC industry impact modifier choices, formulation, and testing.

10.2 WHY USE IMPACT MODIFIERS?

In some rigid PVC applications, impact-modifying additives are not used. For these products, adequate strength and impact resistance can be achieved with the selection of a high-molecular-weight PVC resin as the base material in the formulation. For part strength, the thickness is increased until minimum strength has been achieved.

Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

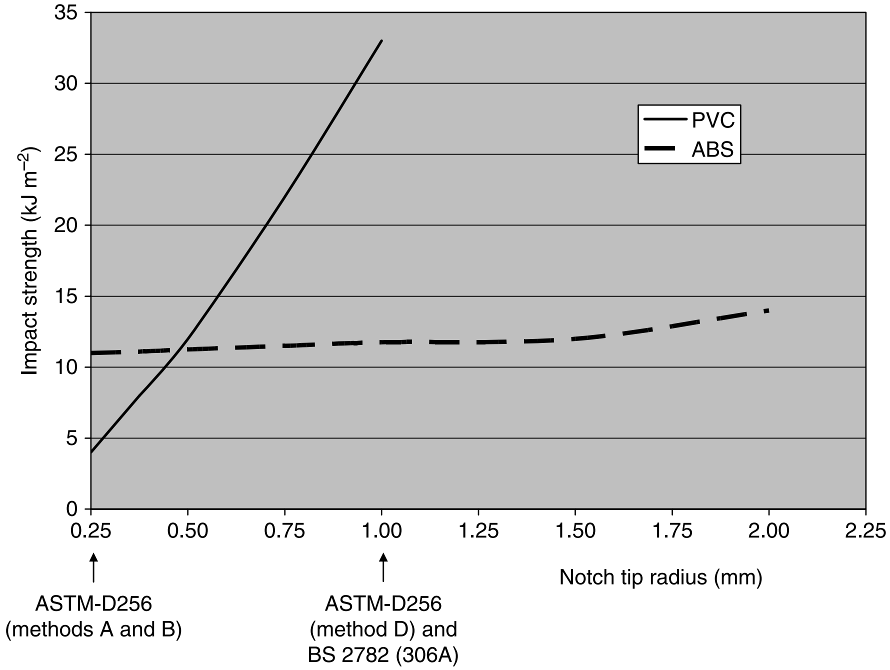

Figure 10.1 Impact strength as a function of notch tip radius.[1,2]

This is often the case in large-diameter PVC pipe. The downside of this strategy is an increase in materials usage and part weight per unit length.

In other areas, the minimization of surface texture irregularities is employed to avoid initiating a crack, which would then propagate through the entire part in a notch-sensitive material such as PVC as shown in Fig. 10.1.[1,2] Textured surfaces such as simulated wood-grained embossing or a traction print can be made as shallow as possible. The downside of this strategy is the softened texture may look less like real wood or have worse wet traction properties.

10.3 IMPACT THEORY

Rigid PVC is an inherently brittle material. As energy is applied to the PVC matrix, a crack can form, especially if initiated at defects such as surface cracks or large filler particles. At the crack tip, a concentrated sphere of plastically deformed PVC forms; this is referred to as the "plastic zone". It is this zone that redistributes the force into the PVC matrix and absorbs impact energy. The zone radius is shown in Fig. 10.2. In the base PVC matrix, this plastic zone can be quite small, and so does not absorb much energy.

To improve impact energy, we want to induce a mechanism to increase the size of the plastic zone. This is where impact modifiers come in. They cavitate or "pop," creating a

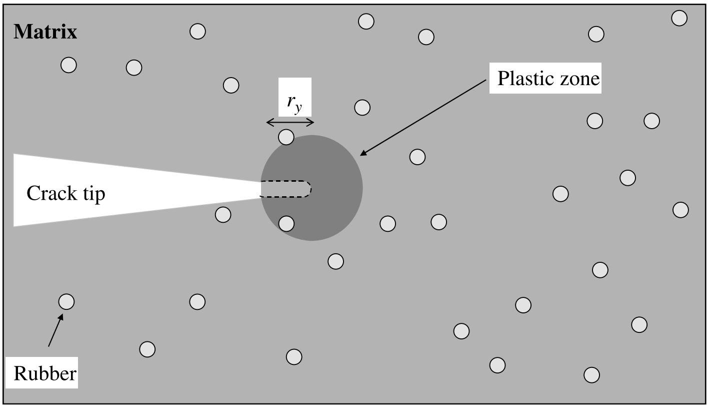

Figure 10.2 Crack tip zone with rubber impact modifier.

change in the stress field. This helps cause one of the two main mechanisms that increase the size of the plastic zone: either crazing or shear bands. Crazes are fibrils of polymer that span the crack as in Fig. 10.3. Imagine two plates of glass with molasses in between. As the plates are pulled apart (a crack), the molasses creates fibrils between the plates, making it harder to separate the glass, and hence absorbing the energy of the "crack." In materials such as polystyrene, impact modifiers induce many crazes to absorb energy. The impact modifier should be approximately 1–3 μm to best induce crazes.

Shear bands are slip zones of plastic deformation that go out at a 45° angle from the crack tip, as shown in Fig. 10.4, and absorb a lot more energy than even crazes. Polymers that naturally form shear bands, such as polycarbonate, are very ductile. Impact modifiers that help induce shear bands should be approximately 0.2–0.5 μm in size. In PVC, impact modifiers can induce shear bands and cause the PVC matrix

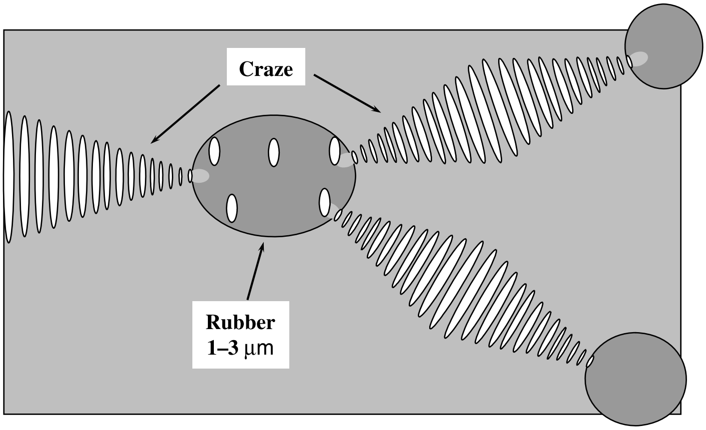

Figure 10.3 Crazing in a polymer with rubber impact modifier.

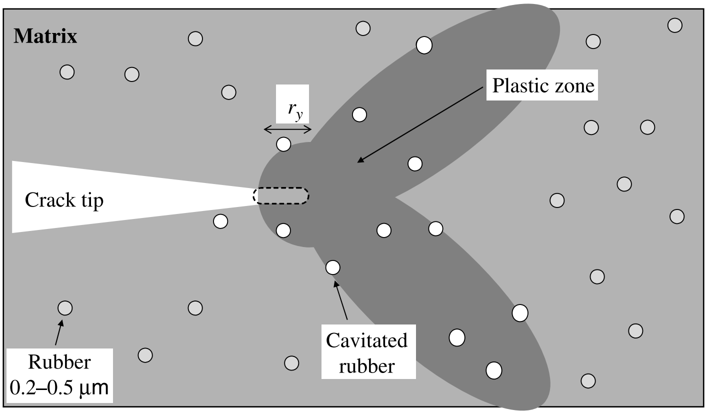

Figure 10.4 Shear band mechanism with impact modifier.

to absorb a lot of energy. In thin parts such as sidings, this is the most likely mechanism. In thick parts such as pipes, crazes are more likely. In both cases, they can be viewed as an increase in the plastic zone before the crack tip that absorbs the kinetic energy of the crack. For more details on these mechanisms, see the excellent book by Kinloch and Young.[1]

The critical factor for all impact modifiers is that they cavitate, forming a hole of the proper size. This means that even inorganic materials can serve as impact modifiers, if they are small enough and can be dispersed properly (a difficult task). An example is the case of calcium carbonate particles dispersed through the PVC matrix: the interfacial adhesion is poor, and the filler, acting as a flaw in the matrix, falls out during cavitation, forming a "hole" (actually a spherical void), and the stress concentration produced by the propagating crack is distributed along the inner surface of that spherical void where the filler once resided. This redistributes the stress over a larger volume. If, however, the filler is large, the hole formed instead helps to propagate the crack. This is why coarse fillers tend to lower impact performance.

What is critical to efficient transfer of crack energy is the proper sizing of this redistribution "hole," which is referred to as domain sizing. For rigid PVC, where shear bands are being induced, this is on the order of 0.2 μm diameter. This makes proper domain size matching critical to the optimal performance of any impact modification system. The domain sizing can be accomplished prior to incorporation into the PVC or during normal PVC processing.

10.4 IMPACT STRENGTH VERSUS IMPACT BEHAVIOR CHARACTERIZATION

An important distinction should be made between these two metrics: absolute impact strength is described in terms of average failure energy per sample thickness, and is expressed as "energy per unit thickness." Impact behavior is usually described as either ductile or brittle and is expressed as a percent of total test failures that failed in a ductile fashion versus those that failed in a brittle fashion, or a "percent ductility." Test methods vary depending upon industry segment, but several popular types include a dropped weight or dart test, where the height of the drop is logged along with the dart or tup weight and the part thickness, and a note is made whether the part suffered a breakthrough (fail) or only a deformation without puncture (pass). A brittle failure is described variously as a sample breaking into pieces or a hole through the sample with a zero angle at any location along the puncture hole rim. Ductile failures are a stretched hole with a fish mouth or round shape.

10.5 VOLUME OF RUBBER

Berard et al.[3] analyzed numerous test results from a large impact modifier testing database and found that, regardless of formulation and lubricant package and processing, the macrotrend suggested that, within similar molecular weight ranges of the base PVC resin, impact strength tended to track as a function of volume of correctly sized rubber domains in the PVC matrix. Increasing the volume of impact modifier improved impact strength through the brittle–ductile transition, shown by the "S-curve" of Fig. 10.5, until fully ductile failure behavior was achieved. At that point, little additional impact strength improvement was noted with further increase in impact modifier levels. This points to lower-density rubber materials having a built-in advantage over higher-density materials, because of greater volume of impact energy dispersion sites.

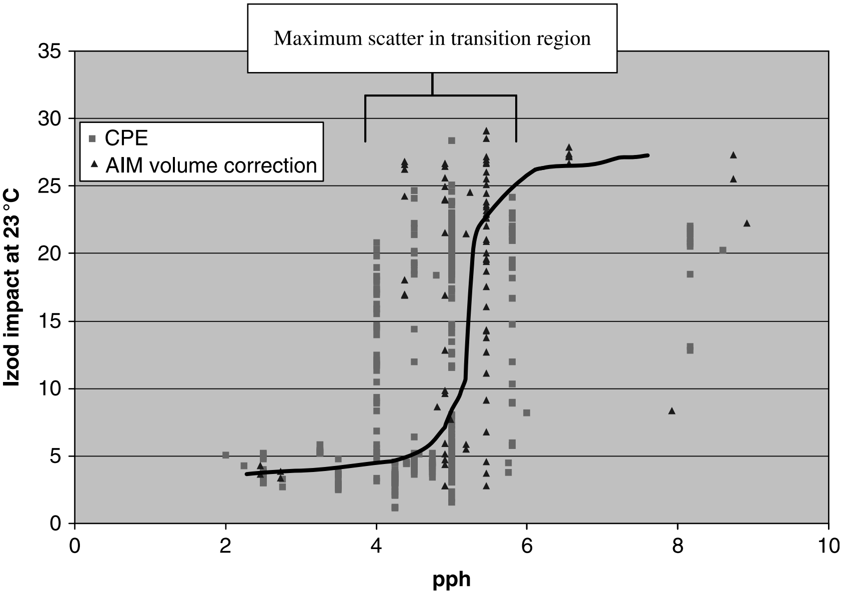

Figure 10.5 CPE and acrylic impact data from LIMS.

10.6 TYPES OF IMPACT MODIFIERS

10.6.1 Presized Impact Modifiers

These include:

- Core–shell rubber: polymethyl methacrylate–butylacrylate (acrylic), methyl methacrylate–butadiene–styrene (MBS), acrylonitrile–butadiene–styrene (ABS)
- Finely precipitated calcium carbonate or other minerals

Core–shell rubber modifiers are a refinement of early attempts to incorporate natural or man-made elastomeric materials into melted PVC. The problems of dispersion and proper domain sizing were improved by the presizing and cross-linking of rubber in a prior manufacturing process such as emulsion polymerization, used to achieve an average 0.2 μm diameter, and then coating the rubber in a PVC-miscible coating (PMMA), normally via copolymerization of methyl methacrylate onto the rubber, followed by spray drying. The coating, PMMA, was originally approximately 40 percent of the total sphere diameter, and more recently 30 percent. Recent advances have resulted in the introduction of a “high-efficiency” acrylic impact modifier with tighter particle size distribution around the desired 0.2 μm diameter, and a minimization of the compatibilizing shell to approximately 15 percent[4] to offer the maximum possible elastomer for a given formulation use level (parts per 100 of resin, phr). The acrylic material has gained broad acceptance as a material with a broad processing window, since it is already sized and readily dispersed in the miscible PVC matrix. In a similar vein, the use of a butadiene rubber as the core offers similar benefits, although with lower thermal stability and higher melt viscosity during PVC processing. For most comparisons in rigid PVC, impact modifier-type core–shell ABS and MBS behave in a similar fashion. The lower T_g of the butadiene rubber ($-90\,^{\circ}$C) versus the butylacrylate rubber ($-50\,^{\circ}$C) may give better low-temperature impact performance. The big drawback for these materials is that the residual double bond in the butadiene is readily attacked by UV light, so these materials cannot be used in weatherable applications.

A recent advance in calcium carbonate sizing technology has enabled precipitated $CaCO_3$ to perform as an impact modifier. Typical mineral filler grades of $CaCO_3$ have ranged from 1.1 μm down to 0.3 μm, with a fairly broad distribution. It is the larger portion of this distribution, well above the desired 0.2 μm/size that causes poor impact performance in rigid PVC. At too large a diameter, the tendency is for the crack to propagate straight past the “flaw” along one side of the “hole” formed by the large particle and continue through the PVC part rather than dissipate energy to the surrounding matrix. These impact modifier grades of $CaCO_3$ form the correctly sized “hole.” Since $CaCO_3$ is not miscible in PVC, there can be an issue with uniform dispersion through the PVC melt, which can be more pronounced as the particle surface area/mass ratio increases (as the $CaCO_3$ is made finer). This issue is usually addressed with the use of surface treatments such as stearic acid.

10.6.2 Process-Sized Impact Modifiers

Some impact modifiers are manufactured in a particle size that promotes ease of handling and then sized down to the 0.2 μm "desirable" domain size during processing. These modifiers include chlorinated polyethylene (CPE) and ethylene vinyl acetate (EVA). The materials are polar in nature and compatible with, but not completely miscible in, melted PVC. This characteristic has an interesting side effect: the impact modifiers form their own domains in the PVC. In the case of PVC that contains mineral filler particles, the CPE or EVA tend to concentrate in the region at the PVC–mineral filler interface—the configuration of lowest energy in the melted mixture. This filler coating keeps the filler from acting as a flaw that propagates the crack. These impact modifiers are sometimes referred to as "filler-accepting," but as mineral filler loads increase, the same amount of impact modifier would form a thinner and thinner encapsulation, finally causing less efficient interfacial energy transfer and a gradual tapering downward of measured impact strength. The filler level at which this point occurs tends to be higher than with presized impact modifiers.

In the case of elastomeric impact modifiers, best results are achieved when the melt viscosity of the impact modifier is a close match to that of the surrounding PVC matrix polymer, an idea described by Taylor:[5] Taylor's theorem (see below). This explains immiscible liquid mixing and describes the ultimate domain size of one liquid (or polymer) in another. It is useful for understanding immiscible polymer blends, and helps explain why some rubber impact modifiers perform more efficiently than others in a PVC polymer of given molecular weight. When the viscosities are properly matched, and the interfacial tension between the PVC and elastomer is low (i.e., these is good adhesion), the rubber domain will achieve the smallest size. In extruded PVC with CPE or EVA, this results in rubber domain sizes of approximately 0.2 μm, which will promote shear bands from the cavitating impact modifier throughout the surrounding PVC matrix.

Taylor's Theorem

$$d = \frac{\Gamma F(\eta_r/\eta_m)}{\gamma \eta_m} \tag{1}$$

where d is the domain size, Γ is the interfacial tension, η_m is the viscosity of the matrix, η_r is the viscosity of the rubber, and γ is the shear rate. $F(\eta_r/\eta_m)$ is a function of the ratio of the rubber viscosity to the matrix viscosity. This function is at a minimum value, 1, when the viscosities are equal, and increases in a parabolic shape as the viscosities are mismatched in either direction. So the rubber domain becomes smaller as the interfacial tension becomes smaller (i.e., the polymers "like" each other). The rubber domains also become smaller as the viscosities of the rubber and matrix are matched. Finally, as the shear rate increases, more shear helps break up the rubber, so the rubber domains become smaller. If these three conditions change, the rubber domain size can change, so correct choices of rubber—both for viscosity and compatibility with PVC—and processing conditions are all important for these types of modifiers.

10.7 FORMULATING RIGID PVC

The formulation development of an impact modifier system must take into account economic considerations as well as performance. In large-scale PVC compounding and processing operations, even small changes in compound specific gravity can result in wide economic swings in either direction. It is strongly recommended to employ a computer software spreadsheet that recalculates total resulting compound volume and numbers of PVC finished goods as lubricants and additives are adjusted. In general, a cheaper lower-density additive (e.g., many lubricants) or very cheap but high-density additives (mineral fillers) improve economics. It should be kept in mind that the base PVC resin has a specific gravity of approximately 1.4, so anything that displaces a portion of the PVC with a material of either lower cost or lower specific gravity is likely to boost savings. There is a practical limit due to lubricant solubility, weathering, die deposits, and so on, which limit the adjustment within a certain range. Typical working formulations for rigid PVC are given in Section 4.2.2.

If a modifier is selected and the goal is to have "drop-in" performance on a set of existing process machines, then several laboratory-scale evaluations may prove useful. The first benchmark to be studied is often a torque rheometer or "fusion bowl" (for details, see Section 18.5). This device is usually electrically heated and has thermoprobes to monitor the compound temperature as the test progresses. A rotor torque reading is recorded as a function of elapsed time as well as the stock temperature. If a compound exists that runs well in a given process (e.g., an extrusion operation), then testing conditions should be chosen that will encourage the compound ingredients to interact in a similar fashion in the torque rheometer as they would in the large-scale process. ASTM recommends 197 °C, 70 percent fusion bowl load factor, and 60 rpm for rigid PVC compounds. The manufacturer of the torque rheometer should be consulted for recommended load factor base upon bowl volume and rotor configuration. This load factor will change as ingredients are substituted, and the specific gravity of the compound should be rechecked to ensure that the load factor remains in the manufacturer's recommended range. If the load factor becomes too great, then material may be forced to remain against the heated bowl interior wall during the test, and may indicate earlier fusion than a properly mixed sample.

Similarly, an underloaded bowl may offer delayed fusion or nonfused powder. The key is to replicate the performance of a standard compound at test conditions close to the melt temperatures encountered in the process. Measurement of the fusion speed at a couple of temperatures that bracket the extrusion temperature can be very instructive, as different formulations will respond more strongly to temperature than others. This is a trial-and-error evaluation that also may vary from instrument to instrument.

Generally, when substituting modifiers, small adjustments to the lubricant package will be necessary to adjust the fusion speed. This will generally involve adjustment of the level of paraffin wax, calcium stearate, and possibly the addition of fusion-promoting agents such as oxidized high-density polyethylene. Running a different modifier without adjusting the lubricant package will often give poor results, especially when changing the type of modifier, for example from acrylic to CPE.

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CHAPTER 11

Processing Aids for PVC

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11.1 INTRODUCTION

Neat PVC resin is a difficult material to form into useful articles using common industrial processing techniques such as thermoforming, extrusion, or injection molding for at least two reasons: first, the polymer resin begins to degrade in the same temperature range where it begins to melt, and, secondly, it tends to stick to hot metal surfaces. Given the fact that most industrial equipment is constructed of metal and that heat is required to shape polymer flow, this could potentially pose a problem. Decades ago, lubricant systems based on metal soaps and hydrocarbon waxes were developed, and the heat stability issue was mitigated with the judicious choice of thermal stabilizers. Processing issues remained, however, and the additives industry was called upon to tackle two areas of concern: melt strength deficiencies and metal release enhancement.

One of the main mechanisms of surface and edge roughness and reduced gloss is shark skin, or slip–stick, processes. The polymer sticks to the die, and as the material exits the die, the free material can move forward without the restraint of the die. If the melt strength, or cohesive energy, is lower than the tendency to stick to the die, or adhesive energy, the polymer will form a tear right at the exit. One can reduce this tendency by increasing the cohesive energy (by increasing the melt strength) or by reducing the adhesive energy (by metal release or slip agents). Both approaches will be addressed in the following sections.

Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

11.2 MELT STRENGTH

Melt strength can be described as the ability of the molten PVC compound to absorb strain forces in the process flow direction. A material exhibiting low melt strength will exhibit "melt fracture" or numerous small tears along the surface perpendicular to the direction of flow, or, in the case of a drawn sheet, may exhibit edge tearing. As sheet extrusion rates and draw-down percentages have increased in the PVC film and extrusion industry segments, the need for improved melt strength has become more pronounced. Melt strength properties of a compound are dependent upon several factors, the most important of which is the molecular weight of the PVC resin itself. Higher-molecular-weight PVC resins have longer chains, which will exhibit a greater number of chain entanglements with other PVC chains in the resin, thus offering an improved resistance to melt tearing. The difficulty is that the high-molecular-weight PVC chains are subject to more shear stress and shear heating, which is damaging to the thermally unstable PVC. What is needed is a high-molecular-weight material that is thermally stable.

A material that increased chain entanglements for the PVC chains or by itself was able to tangle additional portions of the existing PVC molecular chains would increase the PVC melt strength. Intimate contact and miscibility with the PVC matrix would also be a prerequisite, and this set of demands has led to the development of long-chain high-molecular-weight poly(methyl methacrylate) (PMMA) acrylic process aids. Molecular weights are on the order of 10^6 ("medium" molecular weight) to 3×10^6 and higher ("high" molecular weight).

A trade-off is present between ultimate melt strength and ease of processing. Too many chain entanglements might lead to high resistance to flow and high extrusion pressures, machine amperage loads, or surging during extrusion. Increased area of chain-to-chain contact results in additional frictional heating during processing, which speeds fusion, an advantage of process aids. Additionally, because the process aids are miscible with the PVC and therefore intimately mix and promote fusion, they can lead to compounds with improved melt homogeneity.

Several North American and overseas suppliers now offer process aids. The ultimate choice of which is best for a particular application is highly dependent upon final formulation, targeted cost, desired run rates and process conditions, ultimate melt strength requirements, tolerance for additional frictional heating, and amperage loads, among other things. The typical process aid usage level varies according to the application, but it can range from 0.5–1.0 parts per 100 of resin (phr) in a profile or sheet extrusion at moderate extrusion and draw-down rates (as long as no edge tearing is apparent) to 4.0–8.0 phr in PVC foam, where melt strength is critical for bubble size control. For acrylic impact modifier-based formulations, the impact modifier may incorporate a percentage of acrylic process aid as a part of a combination one-pack, thus eliminating the need for a separate addition. For other impact modifiers such as CPE, MBS or fine-grade minerals, this additive must be weighed up and added separately. See Table 11.1 for several commercial grades available in North America.

TABLE 11.1 Commercially Available Process Aids

Manufacturer	Brand	Product	Molecular Weight	Application Area
Rohm & Haas Co.	Paraloid®	K120N	Medium	Profiles, sheet, pipe, and molding
Kaneka Texas	Kane Ace™	PA-10	Medium	Profiles, sheet, pipe, and molding
Arkema Inc.	Plastistrength®	550	Medium	Siding, sheet, profiles, pipe, and blow-molding

11.3 METAL RELEASE

The problem of PVC compound metal release became more apparent as the PVC processing industry began to employ higher and higher output rates and longer and longer continuous processing runs on the same production lines. In earlier years, the hourly buildup of material may have been cleaned off the metal surfaces years before the amount of material buildup had a negative influence on surface quality or processing. This cleaning process may have entailed equipment disassembly and cleaning, or the use of a highly stabilized and filled nonfusing PVC blend known as "purge" material being run through the machinery to scrub the contact surfaces clean from accumulated PVC.

Since the metal release agents function in a similar fashion to "external" lubricants such as hydrocarbon waxes, why not just increase the level of wax and dispense with the extra metal release ingredient altogether? There are two reasons. The first is that wax can slow fusion in the early part of the extruder barrel—a potential negative effect. Metal release agents generally have a neutral effect on fusion speed, yet go to the metal surfaces in the die to give metal release. The other reason for the use of metal release compounds is the potential for "plateout"—die deposit or precipitated material on the edge of a die lip or upon the surface of a sheet takeoff roller due to exceeding the ultimate upper solubility limits of a nonpolar hydrocarbon wax within a PVC melt. The die deposits will accumulate over time and begin to thermally degrade or cause physical surface defects on the finished part as it slides past the die lip deposit or flows across the dirty roller. What is needed is a material that can migrate from the PVC melt to the metal surface and remain in place as the PVC melt moves past it. There are two types commonly employed in PVC today: oxidized polyethylene (OPE) waxes and low-molecular-weight comonomer acrylics. The distinction between external lubricants and processing aids is also discussed in Section 12.1.3; release agents for PVC are discussed in Section 12.5.

Oxidized Polyethylene Waxes These are typically formed in an oxidation tower where relatively large-diameter low-density polyethylene (PE) molecules are introduced into a heated air stream and the PE begins to oxidize. The extent of oxidation is described by a compound's "acid number": the higher the number, the greater the degree of oxidation. In the PVC melt, the oxidized portion of the PE wax molecule is polar and is attracted to metal, whereas the bulk of the low-density molecule is still nonpolar and immiscible in the PVC matrix. During processing, this immiscible material flows to the edge of the PVC melt between the metal processing surface and the PVC polymer melt.

If the metal release agent were a pure nonpolar wax, there would be no affinity for the metal surface, and the wax would flow out with the process flow as a lubricant or possibly out of the melt stream altogether as plateout. The oxidized functional group on the PE wax molecule allows the wax molecule to remain in place at the metal wall while the melt stream continues to flow past. The reason this wax molecule is so effective in this regard is the fact that the low-density PE molecule has a highly branched structure that allows for multiple points of contact with the metal while still allowing nonoxidized chains to push out from the surface. This structure keeps the PVC from getting too close to the metal wall and sticking to the metal, and the multiple points of contact keep the OPE from being wiped off the metal wall by the PVC flowing by. Of course, there are frictional forces removing small amounts of the metal release as time progresses, so the need for a steady stream of replacement metal release as the compound is processed is warranted. The typical usage level in a rigid PVC blend of the OPE low-density wax is 0.1–0.2 phr by weight.

There is an important distinction between OPE wax grades. If the starting PE wax material is a low-density type, then the oxidized functional group is added onto a large highly branched molecule, and this material functions as an external metal release. If the starting material is a high-density PE wax, then the final product functions as a fusion promoter. Again, the basic method of manufacture is the same, and an "acid number" is used to describe the extent of oxidation. An oxidized functional group on a small, dense wax performs in a way to interact with the PVC granule and primary particles before the OPE wax can be rejected to the metal wall. Once the oxidized portion interacts with the PVC resin granule, the PE wax increases frictional heating between PVC primary particles. The result is a fusion speed increase and not metal release at the wall. Low-density OPE wax = metal release; high density OPE wax = fusion promoter. Commonly used grades are shown in Table 11.2 (see also Section 12.2.1).

Low-Molecular-Weight Comonomer Acrylics As a metal release agent, "lubricating" acrylic molecules can intermingle with the PVC primary particles and provide shielding to the hot metal surface. These are different from the long-chain acrylic process aids, and generally contain other comonomers (e.g., styrene). Acrylic molecules are more thermally stable in an oxygen-free environment than

TABLE 11.2 Commonly Used OPE Waxes

Manufacturer	Brand	Product	Base Feedstock	Acid Number	Application Area
Honeywell	A-C	316A	HDPE wax	16	Fusion promoter
Honeywell	A-C	307	HDPE wax	7	Fusion promoter
Honeywell	A-C	629A	LDPE wax	12	Metal release

TABLE 11.3 Commonly Used Comonomer Acrylics

Manufacturer	Brand	Product	Molecular Weight	Application Area
Rohm & Haas Co.	Paralold®	K125	Very low	Profiles, sheet, pipe, and molding
Rohm & Haas Co.	Paralold®	K175	Medium	Profiles, sheet, pipe, and molding
Kaneka Texas	Kane Act™	PA-101	Very low	Profiles, sheet, pipe, and molding

PVC, so as the melt flows past the hot metal surface, the acrylic prevents the PVC from bonding to the metal surface and is able to tolerate the heat load at typical process residence times. The small amount of PVC that does stick to the metal surface despite the presence of the acrylic is scrubbed off by the next wave of acrylic and PVC as the melt continues to flow. Commonly used grades are shown in Table 11.3.

Acrylic release agents in small amounts are generally described as "not affecting fusion characteristics," thus eliminating the need for formulation lubricant adjustments. The polymeric nature of these materials means that plateout is not an issue for these materials. Additional benefits of acrylic release agents may include improved surface appearance.

Several manufacturers have found that a blend of two different types of acrylic metal release agents gives an ideal mix of melt motility and PVC shielding effectiveness; for example, using a low-molecular-weight and a very low-molecular-weight acrylic in a 50 : 50 percent combination at 1.0 phr total.

11.4 FORMULATION DEVELOPMENT, BENCHMARK TESTING, AND STARTING-POINT FORMULATIONS

Why Develop New Formulations? The number one reason in the current industrial climate is for cost savings. As manufacturing sectors mature and as margins become tighter, there is pressure to reduce material costs. Different PVC resin types, heat stabilizer packages, lubricant packs, and increased filler loadings are several common avenues to improve the bottom line. One important caution must be stated: when comparing two formulations for cost, the changes in compound specific gravity must be checked. Even small changes in this number one way or the other multiplied over millions of pounds of compound can result in significant savings or cost penalties.

Another important motivator to revisit formulation development is that increased production rates or revised product specifications have caused a previously approved formulation to no longer fit the bill. As run rates increase, the total heat load due to residence time may go down, resulting in a cold-melt/underfused product. Or, higher shear rates may increase the shear heating of a shear heat-sensitive material, resulting in overfusion or burning. The key here is to understand why the old standard is not performing acceptably in the new production setting and to adjust the new blend to perform better in the proper direction.

How to Develop New Formulations? The answer to this question could fill volumes, but, given the restraints on developmental time and resources in place at most manufacturers, the short answer is this:

- If benchmarking from an old standard blend, list any attributes as well as deficiencies of that standard. Did it offer a broad processing window? Or did it always run only "marginally" well on some lines?
- List the absolute musts of the new blend: must contain 15 phr of filler; must use existing stabilizer package; must save X-dollars annual compound cost.
- Once a candidate is sketched out, consider a financial/density comparison to verify that the cost position is still favorable.
- Blend the test compound and run alongside a standard in laboratory-scale tests (at the minimum fusion bowl, thermal stability, and some type of flow measurement, such as capillary rheometry).
- Evaluate laboratory-scale data, make adjustments as needed, or proceed to a short "box" trial on the process line. Allow the process to come to equilibrium before recording data.
- Evaluate box trial results, adjust further, or proceed to larger-scale trials.

Much time is spent on achieving optimal lubricant balance and fusion characteristics. This process can be very lengthy, but the use of experimental design, controlling the process variables, and an intelligent choice of experimental ranges (knowledge that is gained from years of familiarity with that particular process) can minimize this development time span. It is impractical to suggest a developmental algorithm here, but it should be considered that the optimal formulations will benefit from an even balance of three factors that influence PVC fusion, starting from dry powder and ending with properly fused PVC finished products:

1. *Chemical energy input*: adjust with fusion promoters such as OPE waxes, PE waxes, and/or proper lubricant ratios.
2. *Mechanical energy input*: extrusion machinery clearances, screw design, output rates, and die material friction factors.
3. *Thermal energy input*: heat energy from feed preheaters, extruder barrel band heaters, and frictional heating through the process.

If a PVC processing operation is in place and there is a working PVC dry-blend formulation currently in use, then the work of formulation development can be fairly straightforward. The key is to take note of any existing deficiencies in the performance of the current blend, if any, and formulate a revised compound that mimics the behavior of the current blend under ordinary processing conditions. This exercise is known as "benchmarking" a compound.

In rigid PVC, the industry tends to rely on an electrically heated mixing bowl known as a torque rheometer. A predetermined amount of PVC dry-blended compound is poured into a running torque rheometer that has been heated to a desired testing temperature, and the powder temperature increase and machine torque load are recorded over time. As the powder heats up and then melts, a torque increase is usually seen up to a maximum point, referred to as the "fusion point"; afterwards, the instrument continues to run, and a gradual torque decrease is observed as the PVC compound completely melts. If this process is allowed to continue, there will eventually be a second increase in torque as the PVC begins to thermally degrade and crosslink. Other times, a second peak will precede a rapid drop-off in torque, signifying PVC molecular chain scission instead of crosslinking. The time taken to reach the second torque increase is usually thought of as a gauge of the relative thermal stability that a compound will exhibit in a production process.

The torque rheometer operating conditions and load factors may vary between laboratories, and the debate over which set of operating conditions is "preferred" is not within the scope of this section. ASTM offers some generalized starting point testing conditions for PVC blends in a torque rheometer (see ASTM Method D 2538). Alternatively, it is suggested that powder load factors are chosen in accordance with the operating ranges specified by the instrument manufacturer (remember that this is a mixing device requiring enough head space to ensure uniform heat transfer) and that rheometer operating temperatures mirror the process temperatures encountered in the actual production process. For example, if the polymer melt temperature in an extruder process stream is measured at 185 °C and the exiting melt temperature coming from the die of the PVC is 200 °C, it makes little sense to do all benchmarking at 165 °C. At that low temperature, some of the lubricants used will have barely reached their melting range and the viscosity that they will exhibit in the production process. It is often instructive to try to bracket the processing temperatures, as different compounds will respond differently to temperature. For the example above, this might mean running bowl fusion at both 185 and 200 °C.

Once the standard and new compounds have been tested, it is important to interpret the data correctly. At a given load factor and testing temperature, the compound torque versus elapsed time curve will decrease following the initial charge down to a minimum torque value. The time to achieve minimum torque and the minimum torque value at that minimum point do not have to match precisely, but a significantly higher minimum torque exhibited by one compound over another may forewarn of higher machine amperage and/or melt pressures during extrusion.

The next significant point is the inflection point, where the increasing torque values after the minimum torque are plotted and where the slope of that plot changes sign. The curve is approaching the torque peak or fusion peak at this point. The customary analysis of a torque rheometer data curve is to concentrate upon the actual fusion peak itself, but the present authors have found less variability from sample to sample in considering the inflection points of a series of experimental runs instead of the fusion peak. The difference was 7–8 percent run to run versus 10–12 percent. In experimental designs, this may improve the response factor modeling. Whether the inflection points or the fusion peaks are considered, the ASTM recommendation is to report fusion time differences to within 30 s (e.g., "1.5 minutes").

Some experimenters report end torque values achieved at the conclusion of the bowl run as a double check to ensure that crosslinking or material change has not already begun, even in the short time that it takes to complete a fusion bowl exercise (approximately 6–8 minutes). These values are useful mostly as a double check, and are not greatly indicative of what happens in a production process, since the average residence time in a counter-rotating twin screw is usually less than 2 minutes at typical industrial extrusion rates.

Each experimenter will eventually discover the inherent variability of back-to-back runs of a standard blend as a "personality trait" of his/her particular instrument. The important thing to understand is what constitutes a "meaningful" difference on that instrument. This machine-specific knowledge usually comes after numerous laboratory runs.

While fusion bowl performance is a critical parameter to those who rely on laboratory-scale testing to guide formulation development, another important yardstick is a characterization of the flow properties of a PVC compound. Most rigid PVC is forced through a shaping die or calibration device, and a good approximation of this behavior on the laboratory scale may be found in the capillary rheological profile. Fused PVC is remelted and forced by a hydraulic plunger to flow through a thin passage in a heated barrel die over a range of different shear rates. PVC compounds tend to shear-thin, and the complete picture of the compound viscosity from low shear rates of about 5 s^{-1} to the highest shear rates likely to be encountered in an extrusion process, about 150–500 s^{-1}, can be compared on a logarithmic scale.

Two compounds that offer significantly different responses especially at the lowest shear rates may not perform the same in a given process. Too high a viscosity at low shear compared with the standard may result in preferential or uneven flow in the edges of a sheet die (too much center flow) or poor material throughput in narrow passages or die corners. Too low a melt viscosity compared with the standard could exhibit "wide running" on a sheet line, with the melt extending out to the far edges of the take-off rollers. For a generalized goal, it is reassuring for the new blend to measure within 10–20 percent of the standard, assuming that the standard offered acceptable performance.

Other benchmark tests are currently in favor at various suppliers and manufacturers. These may include heated two roll-mill testing to check flow and surface qualities, notched impact testing on laboratory batches pressed into plaques, bulk and specific gravity testing of powders, color measurements, and others. If the experimenter has a high confidence level in a particular testing regiment that is not described here or performed differently, then he/she should by all means proceed accordingly! The point is to test compounds properly and to interpret the results of "key" tests correctly rather than go through a lengthy battery of laboratory exercises and experimental runs which give inconclusive or contradictory results.

Starting-Point Formulations—The Basics These are generalized, and any actual starting-point formulation under consideration should be compared with the performance of an existing standard blend that runs acceptably on the current process—or, if developing a new formulation from scratch, one should check the output variables against the expected standard and make adjustments and substitutions accordingly (see also, Sections 4.2.2 and 12.3).

PVC pipe in the United States is characterized as either drain, vent, waste (sanitary) pipe (DVW pipe) or as other pipe not intended to carry potable water. Ingredient range compositions and a list of qualified alternative ingredients are specified by the Plastics Pipe Institute (PPI). In the formulation shown in Table 11.4, the first ingredient specified is the PVC resin. Generally, a grade is chosen as the best compromise between finished part performance (higher molecular weight is generally superior) and ease of processing (lower molecular weight tends to process more easily). The industry frequently selects a free-flowing powder with a 150–200 μm particle with $K = 65$–68. For correlation of K-values with intrinsic viscosity and actual molecular weight, see Chapter 2, Appendix 1.

Calcium carbonate, limited by the PPI to 5 phr, may or may not be surface-treated with stearic acid to improve handling and dispersion. Generally, a smaller calcium carbonate particle is obtained through a precipitation process (0.3–0.7 μm), and smaller particles tend to offer better impact strength than ground calcium carbonate (1–3 μm or larger).

Titanium dioxide is used to give opacity and white color to pipe and to provide some protection against UV damage, which causes PVC to turn yellow. Since sanitary pipe may sit out in the sun at a construction site or during storage prior to installation, some protection is desirable to avoid the appearance of discolored pipe.

Paraffin wax is a by-product of petroleum refining operations and is a lubricant that prevents PVC from sticking to metal surfaces during processing and provides the essential wall slip in the extruder and die. There are many paraffin grades available as pure single materials and as blends of waxes. Generally, hydrocarbon waxes are described by their "drop" temperature, the point at which the wax begins to liquefy. Typical drop temperatures selected are in the 165 °F (74 °C) range for rigid PVC processing. Often, increased paraffin levels translate to slower PVC fusion in a given formulation (see Section 12.2.1).

Calcium stearate, categorized as a "metal soap," is both a lubricant and a secondary stabilizer. In European applications, lead, zinc, cadmium, and calcium stearates provide lubrication and heat stability to PVC; lead and cadmium are being phased out. The calcium stearate acts as a mild fusion promoter in most cases; however, at high usage levels, the behavior can change character, and further increases in calcium stearate may actually delay the onset of PVC fusion.

TABLE 11.4 PVC Sanitary Pipe Formulation

PVC resin $K = 65$	100 parts
Calcium carbonate	5
Titanium dioxide	1
Paraffin	1
Calcium stearate	1.2
Heat stabilizer	0.75
Acrylic process aid	0.5

Heat stabilizers in North America are primarily based upon methyl or butyl tin mercaptides, and numerous offerings are currently available in the marketplace. The general rule of thumb is that the higher the percentage of tin by weight, the more effective the stabilizer tends to be. Other systems may employ a combination of tin and silica zeolite mineral as a co-stabilization scheme. One important feature of stabilization systems is that lead and tin systems do not mix, so care must be taken when switching from one to the other to avoid PVC blackening. Calcium/zinc and barium/zinc systems are compatible with either tin or lead.

Note that this DVW pipe formulation contains no impact modifier or other lubricants. Depending upon the desired finished properties of the pipe, the minimum impact strength standards may be achieved simply by increasing the wall thickness of the pipe specimen. Other lubricants may improve processing and fusion speed but may add cost.

Compared with sanitary pipe, irrigation pipe contains far greater levels of mineral filler (see Table 11.5). This may increase the rigidity and heat distortion resistance of the finished product. If these were both run in a process, the operator may note that the higher filler loading appears to act as a heat sink, thus delaying the onset of PVC fusion. As a result, hotter processing temperatures or fusion-promoting lubricants may be required. At these usage levels, it will be very difficult to achieve acceptable filler dispersion in the PVC melt, and there may be system powder handling problems (blocking and dusting) as well, so a finely precipitated calcium carbonate grade that has a stearic acid surface treatment is a must.

Why has this formulation been labeled as irrigation pipe or fence substrate. There are many similarities between the two products, and since PVC fence is currently considered a high growth market in North America, several former pipe makers have converted their operations from pipe to fence, even retaining the older pipe dies (square) fed into a rectangular or square final calibrator.

Higher levels of mineral filler will lessen finished part impact strength, so a rubber impact modifier such as chlorinated polyethylene, MBS or acrylics may be necessary. The material cost savings realized by using 25 phr of filler more than offsets the increment cost increase of an impact modifier in this case.

Finally, note that in the basic starting-point formulation is Table 11.5, the lubricant levels have been increased slightly, to counteract the “dry” running of large amounts

TABLE 11.5 PVC Irrigation Pipe/Fence Formulation

PVC resin $K = 65$	100 parts
Calcium carbonate	25
Titanium dioxide	1
Paraffin	1.1
Calcium stearate	1.4
Heat stabilizer	0.75
Acrylic process aid	0.5
Impact modifier	3

of mineral filler. The calcium stearate has been increased more than the paraffin to promote fusion at these high filler levels.

Next to PVC pipe, the major application for rigid PVC is vinyl siding (see Table 11.6). This product is a coextruded offering, with 85 percent of the part weight being found in the underlying substrate. Unlike PVC pipe, there is a limit to the thickness due to finished part weight requirements. This limits filler type (there is a need for fine precipitated, surface-treated grades) and usage level. At a thickness of 40–50 mil (1.0–1.3 mm), the vinyl siding sample needs an impact modifier to achieve minimum impact standards. These standards are regulated by the Vinyl Siding Institute in the United States or the Canadian Siding Institute in Canada. Unlike pipe, siding may still be marketed that does not meet these certifications, but contractors and re-modelers generally stick with certified products.

Another important difference between PVC pipe and siding manufacturing operations is "line speed" or extrusion rate. While pipes and profiles are described as running several "feet per minute," line speeds in siding can reach up to 150 ft/min (0.76 m/s). This results in a very short residence time of the PVC blend, which often moves through the entire line from feed throat to exiting the die in less than one minute. Therefore, vinyl siding producers are perpetually fighting cold-running or underfusing material in contrast to pipe. The choice of lubricants in vinyl siding tends to include one or more fusion-promoting ingredients or a balance of paraffin and stearates that offer faster fusion.

PVC siding is a co-extrusion, while profiles tend to be monolayered offerings. The functionality is similar, with stringent appearance and color-hold requirements, resistance to marring or impact damage, and acceptable processability. Window profiles are run much more slowly on the extrusion line than siding, but since siding substrate is run at a relatively high extrusion rate, how is it possible to get adequate fusion in the capstock that must be run at the same high speed? Table 11.7 shows a starting-point formulation for profiles/capstock. Generally, capstock formulations are run much hotter than substrate extruders. The balance of lubricants and ingredient choice are also critical to this success. There are other additional colorants and titanium dioxide amounts desirable in the case of nonwhite capstocks, but for window profiles the color is mainly white. In dark colors, a "non-chalking" titanium dioxide grade (which usually means the titanium dioxide has a surface coating preventing chalking) is usually specified so that additional (expensive) colorant is not required to prevent

TABLE 11.6 PVC Siding Substrate Formulation

PVC resin $K = 65$	100 parts
Calcium carbonate	15
Titanium dioxide	0.5
Paraffin	1.1
Calcium stearate	1.4
Heat stabilizer	0.8
Acrylic process aid	0.75
Impact modifier	4

TABLE 11.7 PVC Profiles/Capstock Formulation

PVC resin $K = 65$	100 parts
Calcium carbonate	5
Titanium dioxide	9
Paraffin	1.1
Calcium stearate	1.4
Heat stabilizer	0.8
Acrylic process aid	0.75
Impact modifier	4

"washout" during weathering. (See also Section 5.3.2 on colorants and Chapter 22 on rigid PVC extrusion.)

Considerable attention is paid to profile "die swell" and "shrinkage" and part of the solution to manage these undesirable traits are the final adjustments to a formulation. Higher PVC resin molecular weights, higher processing temperatures, higher extrusion rates, lower filler loadings, and even impact modifier choice and usage level all may have an effect upon the final degree of die swell. Die swell refers to a part's dimensional change after it exits an extrusion die. The term shrinkage refers to post-processing dimension change as the finished article sits on a shelf or after installation.

With all of these starting-point formulations the following decision-making process may be useful:

1. Check the formulation against the stated goals at the outset of development work.
2. Validate performance versus standard on laboratory-scale analyses.
3. Check economic calculations (which must include formulation density changes).
4. Run a sample on a production line for long enough to reach the equilibrium processing state.
5. Evaluate appearance, physical characteristics and so on, versus requirements.
6. Monitor performance during longer plant trials to ensure that performance expectations are achieved.

CHAPTER 12

Lubricants and Related Additives

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12.1 CHARACTERISTICS OF LUBRICANTS

It is difficult to define “lubricant” other than in terms of function. A lubricant is an additive that provides a measurable decrease in the resistance of polymer chains or chain segments to movement in relation to other polymer chains or to objects (filler particles or processing equipment surfaces) in their vicinity, at a relatively low level, without introducing more than minor changes to other observable properties. The implication is that there will be little change to the glass transition temperature of the polymer.

Many lubricants have other functions. Often, antioxidants and heat stabilizers have some degree of lubricant behavior. In many cases, it is likely that antidegradants form complexes with lubricants, or associate in the polymer matrix with them. It is useful for the formulator to think in terms of a mobile additive system designed to put the right ingredient in the right place at the right time. A classic example is the combination of organotin stabilizer with calcium stearate and paraffin. It is likely that the three travel together: stearate groups in close proximity to paraffin, carboxylate groups complexed to the stabilizer. Antioxidants bearing nonpolar alkyl groups probably also complex with lubricants. Antioxidants and heat stabilizers are expected to influence observed properties, that is, to provide stability. Physical evidence of lubricants after processing is complete is, on the other hand, usually not desired.

12.1.1 External and Internal Lubricants

In PVC processing technology, a distinction is drawn between internal lubricants, which facilitate movement of one polymer chain with respect to others, and external lubricants, those facilitating movement with respect to solid interfaces, usually the surfaces of processing equipment. It is not always easy to establish the distinction. It is, for example, not clearly related to chemical identity. Paraffin wax behaves as an external lubricant in PVC but as an internal lubricant in polyethylene. A statement that a given additive is one or the other must be accompanied by reference to a specific polymer and, often, qualified that it functions primarily in one regard. The classification is most often deduced from limited data. If a lubricant appears to have improved flow in a particular process, but cannot be found on the surface to a greater extent than throughout the composition, it is considered internal. If it is noticeable at the surface, or appears to have modified surface properties, it is thought to be external. If observations are contradictory, it may be classed both ways. If it is clear that both functions are involved, the additive is routinely termed a “balanced,” “combination,” or “multifunctional” lubricant. These distinctions, again, are meaningful only with reference to a specific composition.[1]

12.1.2 Lubricants and Plasticizers

Addition of plasticizer to an at least partly amorphous polymer also promotes movement of chains and chain segments. Plasticizers, however, are not normally used in trace quantities (when they are, it is often as lubricants, such as trace additions of ester plasticizers to semicrystalline polyolefins). In addition, significant changes to properties of the composition, reflecting alteration of the glass transition temperature, are anticipated. The improvement to polymer flow in some flexible vinyl compounds may be so great that addition of lubricants may not be needed. Further, the mobility of other additives may be promoted by plasticizer solvation to the extent that complex formation with lubricants is not essential to their operation. In practice, these instances are rare. More common is the situation where the presence of a substantial amount of plasticizer enables species not routinely considered lubricants to act in such a manner (instances will be discussed in the following). In plasticized polymers, dispersion (van der Waals) forces and hydrogen bonding interactions between polymer chains (which provide rigidity and strength, as well as impeding flow) are partly replaced by interaction between the polymer and functional groups of the plasticizer.[2]

The plasticizer also contains noninteractive sections that have weak nearest-neighbor interactions. Plasticizers have been described, by analogy, as nonvolatile solvents.[3] Although the statement means solvent for the polymer, the plasticizer, in addition, should be a good solvent for many additives. It is expected that the interactive part of the plasticizer will have strong attraction to a polar section of the polymer and not be easily displaced. The noninteractive section of the plasticizer may have some attraction to the less polar part of the polymer and may assist in solvation of additives. The main role of the plasticizer, however, is conversion of intermolecular attraction from strong polymer-polymer forces to weak (plasticizer + polymer) $\leftrightarrow$ (plasticizer + polymer) forces. Plasticized polymers may be thought of as intermediate stages between the pure polymer and a solution in a good solvent. The interactive part of the lubricant, although it must similarly coordinate to a section of the polymer, must not interact so strongly as to lose mobility during processing (otherwise it becomes a minor and probably ineffective addition of plasticizer). To facilitate this, the noninteractive section of the lubricant is usually chosen to be incompatible with the polymer, that is, to have a solubility parameter that is lower by 2–3 $\text{MPa}^{1/2}$. With polar polymers such as PVC, this range is provided by saturated aliphatic hydrocarbon groups. The nature of the interactive part of the lubricant varies greatly, depending on the application. In summary, although a plasticizer can provide the function of a lubricant, a lubricant normally does not act as a plasticizer. The type and level of plasticizer may, however, greatly affect how a given lubricant behaves.

12.1.3 Lubricants, Processing Aids, and Other Additives

A processing aid is (obviously) an additive that facilitates a given process. Thus, in certain mixing or calendering operations, offspec or trim compound is used as a processing aid. Additives sold commercially as processing aids normally help several processes: mixing, fabricating, etc. For PVC, the most commonly used processing aids are compatible polymers that tend to relieve restrictions to chain and segment motion imposed by a particular molecular weight distribution. This is done by forming an internal microphase, containing both polymers, in which a great deal of polymer chain motion is possible, without the phase being extensive enough to greatly alter the glass transition temperature of (i.e., to plasticize) the base polymer. In many cases, a beneficial alteration (e.g., impact toughening) is discovered. In others, the composition is simply easier to process. In rigid PVC, absence of plasticizer emphasizes the need for processing aids. Despite the foregoing, the distinction between a polymeric plasticizer and a processing aid is not always easy to draw. The most effective processing aid (using the term in the broad sense) in flexible PVC is the plasticizer (here, it should be noted, a reduction in glass transition temperature is desired). A lubricant will often act in concert with a processing aid. Additives that behave like, or act in concert with, internal lubricants are generally referred to as “processing aids.” Those that behave like, or act in concert with, external lubricants are termed “lubricating processing aids.”

A release agent, on the other hand, is often a lubricant. There are many instances where it is desired that an additive promote external lubrication (i.e., decrease the interaction between the compound and a surface) briefly, such as in flow through a runner or die, and then disappear into the composition, becoming unobservable. In other cases, it is desired that the action persist slightly longer, perhaps sufficiently to facilitate part removal from a mold. In this case, the external lubricant (vis-à-vis mold flow) becomes a release agent (with respect to mold opening and part removal). Commonly, it is desired that the release agent vanish into the composition on standing. In other cases, its surface persistence may be tolerable. In some instances, it is desired that the additive be actively present on the surface, decreasing the coefficient of friction. In this case, it is termed a slip agent. Ethylene bis-stearamide (EBS) is commonly used in PVC to provide external lubrication during processing, followed by service as a slip agent. This may be complicated by formulation with additives that are poor lubricants, but good release or slip agents, borne to the surface during processing by others that are good external lubricants. Some additives, designed primarily as release or slip agents, may function as external lubricants in flexible PVC in cases where the need for internal lubrication is minimized by plasticizer type and level. There may be, therefore, some functional overlap.

It should be emphasized that assignment of specific function to a given additive is always a first approximation. It is the entire additive package that must be characterized as providing lubrication, release, or processability. The entire additive system must also be assessed regarding any other surface effects desired. For instance, an external lubricant may be expected to interact with, and help bring to the surface, polar, hygroscopic additives that develop a hydrogen-bonded surface network that can drain accumulation of static charge to a ground. In some cases, it may be difficult to distinguish lubricant and antistatic function; the formulator must visualize both simultaneously.

12.1.4 Internal Lubrication and Viscosity

The effectiveness of an internal lubricant is typically judged by noting the extent of reduction of melt viscosity. The meaningful measurement of viscosity of non-Newtonian fluids requires apparatus with controlled geometry. Two genre are popular: those whose geometry is simple enough to yield a true viscosity, such as parallel plate and cone/plate viscometers, and capillary rheometers, all of which may be adjusted to particular shear rates; and, secondly, devices that measure a reflection of bulk viscosity, such as torque or power draw. These duplicate the shear rate of a particular process by being constructed as miniature models of production equipment. They do not apply to as broad a range of viscosity as the first category, and yield only relative values, but, within these limitations, are very effective and, therefore, in widespread use.[4] In the ideal case, the viscosity of the polymeric composition (at the process temperature, and at a shear rate comparable to that of the process) is stable with time. Viscosity decrease versus concentration of internal lubricant is then easy to observe. It is less so with polymers such as PVC, whose decomposition temperature is in the same range as the melting point. Measurements in almost every case must, therefore, be obtained on PVC compositions containing heat stabilizers. The behavior of the latter is influenced by the type and level of lubricants. The effectiveness of lubrication also depends on the stabilizer providing processing time prior to viscosity change from decomposition. Despite these cautions, it is often possible to compare a series of additives in a specific PVC compound and obtain a judgment of their relative effectiveness in reducing process viscosity.

12.1.5 Measurement of External Lubrication

With external lubrication, concern is focused on the interface between the compound and the process equipment. The surface of the latter is generally an oxidized polar layer with a pattern of microscopic cracks and pits. The polar sections of external lubricants are adsorbed on this layer and in these sites. Compound flow at the lubricated surface is then hindered only by the interaction of nonpolar ends of lubricant molecules adsorbed on the surface with others borne by the polymer. The primary effect is less resistance to flow; secondary effects may include higher output, lower heat buildup and energy consumption, improved surface appearance, and easier release. The effectiveness of an additive as an external lubricant should be determined with laboratory-scale equivalents of the process equipment. Small extruders, calenders, and spiral flow molds are commonly used. Lubricant concentration is then related to output, appearance, and power draw at various conditions of temperature and machine speed. Alternatively, the process is simulated with a torque rheometer. All of these experimental procedures usually measure both internal and external lubrication; that is, they are intended to solve specific practical problems rather than categorize effects.

Methods that duplicate factory processes are also vital in spotting undesirable side effects that may result from excess external lubrication. There is usually no need for more than a monolayer of lubricant on the processing equipment surface to interact with polymer molecules flowing past. Equilibrium between the internal concentration of lubricant and the extent of adsorption on the processing equipment surface is to be expected. But, just as flow is not always streamline, equilibrium in adsorption phenomena is not always reached. A point of high stress (e.g., an orifice, a die, or a nip) that induces increased deposition of external lubricant by lowering its compatibility with the polymer may not always be followed by a zone in which the composition has sufficient time, under reduced strain, to resolvate the excess lubricant. A permanent deposit, generally termed plateout, results. As this builds to multiple layers of lubricant, polar groups, normally adsorbed on the metal surface, now protrude. These induce further deposit of polar ingredients, and finally of the entire compound.[5] With passage of time under such conditions, no level of stabilizer can prevent degradation and resinification of such deposits. Clearly, overlubrication must be avoided to prevent such effects, recognizing that "overlubrication" is a function not only of how many parts of which lubricant was used, but also of relevant equipment design. What proves overlubricating on one process line may not be with another. The tendency to form multiple layers is, in addition to considerations discussed above, a function of the magnitude of the interaction between the nonpolar sections of two lubricant molecules (the one adsorbed to metal, the other at the surface of the compound). A low level of interaction tends to correlate with the lubricant itself, or its solutions, having low viscosity. This observation has led to simple laboratory screening tests.[6]

Sometimes, the opposite occurs. New or refinished machinery often (temporarily) has process surfaces much smoother than what was replaced, leading to insufficient deposition of external lubricant. As a result, the break-in period of running at reduced output on new equipment may far exceed that anticipated. Similarly, there may be a temporary drop in output associated with a change in formulation, as one external lubricant slowly desorbs another from the equipment surface. These factors tend to escape notice in the laboratory because of the small size of the equipment. The successful innovator, either of process or of composition, is, however, one of patient persistence. It should not be presumed that addition of lubricants, even at correct levels, will never involve compromise. Reduction in bulk viscosity by internal lubricants may be expected to have a minor (but not zero) effect on glass transition temperature. Additives that function as heat distortion temperature improvers and impact strength modifiers are rarely lubricants, and vice versa. External lubrication must often be balanced against interference with subsequent coating, printing, or heat sealing, realizing that total readsorption into the compound after processing, even when the predominant mode, is a first approximation.

12.1.6 Lubricants and Fillers

Polymer molecules are expected to flow by solid surfaces such as gates and runners, and dies and nips. They are not expected to flow by filler particles and leave them behind, even though it is clear that a certain degree of polymer chain and segment movement will be needed in the vicinity of the polymer–filler interface as the composition flows. It is possible to choose polymer–filler combinations in which the polymer wets the filler so poorly that processing causes fractionation of the mixture, but this is rarely intentional. At rest at ambient temperatures, the filler particle serves as a physical crosslink, comparable to a point of strong polymer chain interaction in a polar polymer such as PVC. During flow, these "bonds" continually break and re-form, the resistance to this finding expression in the increase in process viscosity caused by the filler. This increase may be countered by addition of lubricant specifically (or serendipitously) intended to be adsorbed on the filler surface. It is a semantic rather than a technical question whether such an additive is internal or external. Most fillers have higher-energy surfaces than that of PVC[7] (those that do not, e.g., PTFE powder, are not easy to incorporate). In consequence, lubricants for use in treating fillers tend to have very polar interactive sections, such as acid, amide or carboxylate anion ligands. As regards PVC polymer, they are more likely to be internal than external lubricants.

With choice of filler treatment, the formulator must typically consider factors other than effect in promoting flow at the proper level. These include heat stability, resistance to various environments, and possible toxicity. Other things being equal, additives for adsorption on fillers should be chosen to have interactive functional groups as similar as possible to those on the filler surface. Therefore, reactive silanes should be considered for surface treatment of silicas, silicates, alumina, or aluminosilicate (clay) fillers. Reactive silanes are not normally considered lubricants, but their lowering of the surface energy of siliceous fillers enhances compound flow by the standard lubricant mechanism of a relatively nonpolar organic section interacting with the analogous section of an internally lubricated polymer. Similarly, if the filler (or colorant) were titanium dioxide or barium titanate, reactive organic titanates should be considered. Where the filler is a metal salt such as a carbonate, metal carboxylates are useful. Evidence has appeared that use of the same cation—that is, for example, calcium stearate with calcium carbonate, but magnesium stearate with basic magnesium carbonate—provides the best processing.[8] Whether to rely on one lubricant for multiple functions, in this case, internal lubrication and filler treatment in PVC, or to use blends of several, will be discussed below. Use of coupling agents is discussed in Section 6.7.

12.2 TYPES OF LUBRICANTS

12.2.1 Hydrocarbons

Paraffin wax, derived from refined petroleum or Fischer–Tropsch synthesis, is the most prevalent external lubricant used in PVC. This additive features low cost, good color, low toxicity, and reasonable stability. Although nonpolar, paraffin wax is polarizable at branch points and trace unsaturated linkages. Unbranched segments tend to form crystallites (or at least domains of high regularity). Branch points and unsaturated groups lie outside these domains. This results in paraffin wax having two sections: one contains regularly oriented long-chain alkyl groups having very low PVC compatibility; the other is a polarizable amorphous section able to coordinate with PVC. There is likely to be specific attraction between polarizable sections of paraffin with unsaturated sites on the polymer. Since the latter are associated with labile chloride, this interaction leads the lubricant to a potential point of degradation. The long-chain alkyl groups in paraffin coordinate with stearate groups from, for example, a calcium stearate/organotin stabilizer complex. Thus, a lubricant/stabilizer additive complex is enabled to navigate to the most useful location. In the complex, polar elements of the stabilizer coordinate to the —CHCl— link, nonpolar elements to paraffin and to —CH=CH— groups. At a point of high stress in processing, nonpolar elements of the lubricant/stabilizer complex also interface with lubricant molecules adsorbed on the equipment surfaces. In the ideal process (i.e., one that produces an article without vinyl degradation), the components of the lubricant/stabilizer system can be visualized as Maxwell demons, cooperating to draw the compound through a tight spot without damage. In a real process, the lubricant/stabilizer system provides sufficient damage control to enable a saleable product.

The related use of paraffin and similar species to control PVC fusion is discussed below in connection with metal carboxylates.

Refining of petroleum yields paraffin waxes having softening points of 55–75 °C; Fischer–Tropsch synthetic waxes soften at somewhat higher temperatures. Polymerization of ethylene to low-molecular-weight (MW) LDPE (density 0.92–0.94 g/cm^3) provides similar products with softening points of 85–115 °C. Low-MW HDPE (density 0.94–0.97 g/cm^3) products, with softening points of 125–140 °C, are also produced. As the product becomes more crystalline, with higher density and softening point, it functions more externally in PVC. Under controlled conditions, the chain ends of synthetic waxes or low-MW PE can be oxidized to acid groups. This improves compatibility with PVC. The major use of oxidized low-MW PE (OPE) is to improve receptivity of a PVC product to printing or other postfinishing processes. In rigid vinyl, the natural high surface energy of PVC becomes unavailable because of the presence of paraffin wax. The combination of paraffin wax and OPE leads to a printable surface. Oxidized Fischer–Tropsch wax can be used similarly. Both are also common in flexible PVC applications where printability is desired, and in wire insulation to aid in clean release from the conductor in making terminations.

OPE is also an excellent binder for dispersions of pigments or other solid additives for PVC. The pigment is more polar than either polymer; PVC is more polar than OPE. Thus, there is thermodynamic drive to transfer the active ingredient from the binder to the polymer matrix. This is an important consideration in formulating dispersions.

Low-MW EVA copolymers are also produced. These have broader solubility parameters than low-MW PE, and are usually multifunctional lubricants. They are valuable as lubricants and compatibilizing agents for PVC/NBR and PVC copolymer/EVA blends.

Paraffin wax can often be replaced with a lower-MW variant, refined mineral oil. It is often convenient to use liquid mineral oil instead of flaking or melting wax. Mineral oil is also used at low levels to externalize other additives, such as antistatic agents, biocides, or release agents.

12.2.2 Carboxylic Acids

Carboxylic acids are generally associated by hydrogen bonding in nonionic media, either with themselves as dimers or as one-to-one complexes with other additives, including metal carboxylate salts and amides. In rigid PVC compounds, species such as stearic acid that do not penetrate the resin granule as rapidly as calcium stearate,[9] may nevertheless complex with it. A more common use is in lead-stabilized PVC, where it reacts with surface Pb—OH groups to form lead stearate groups, useful in displacing labile chloride and improving early color. In such systems, stearic acid content can be used to adjust fusion time.

Commercial "stearic acid" comprises a blend of C_{14}–C_{18} even-numbered, straight-chain aliphatic acids derived from animal fat or vegetable sources (the latter provide Kosher stearic acid). It is refined to low residual unsaturation in the interest of good heat aging characteristics and may contain minor amounts of antioxidant such as BHT. Montanic acid, a blend of C_{26}–C_{32} acids from lignite, having very low unsaturation but of higher cost, can be used instead. If use of the acid as a filler treatment is desired, such as with alumina trihydrate (ATH) or magnesium hydroxide, improved processing may result from the use instead of 12-hydroxystearic acid. In flexible PVC, stearic acid is a common ingredient in filled formulations. When filler surface treatment is desired, the additive should be incorporated with the filler rather than later. In clear and translucent compounds, stearic acid is often replaced with liquid ingredients, such as isostearic and tall oil (oleic) acids. The latter are particularly valuable in improving air release from plastisols and contributing to uniform cell structure in foamed plastisols.

Because of their ability to form mobile dimers, stearic and related acids can be highly migratory. This is useful in aiding release of wire insulation from the conductor, but may interfere with postfinishing processes such as printing or decorating of film. Replacement with a combination of OPE and an ester lubricant has been recommended.[10]

12.2.3 Alcohols

Commercial blends of C_{16}–C_{18} aliphatic alcohols are referred to as cetyl alcohol if C_{16} predominates or stearyl alcohol if mainly C_{18}. Both have good color and heat stability, but are relatively expensive. The major use is at levels of 0.2–0.5 parts per 100 of resin (phr) in conjunction with dibasic lead phosphite and tribasic lead sulfate stabilizers. The complexes formed aid mobility of these stabilzers without disturbing fusion time. A similar effect is found with metal oxide fillers and with the desiccant calcium oxide. The latter should not be used with stearic or other acid, since it would be converted rapidly to calcium stearate during processing. Similarly, the scavenger polycarbodiimide (PCD) should not be used with stearic acid.

12.2.4 Amides

Simple primary amides such as stearamide, oleamide, and erucamide are widely used in polyolefins and styrenics as lubricants, but mainly in vinyl as release agents, discussed in the following. Aliphatic amides are strong enough nucleophiles (at process temperatures) to detract from the heat stability of PVC, and are therefore used at low levels or in situations where heat aging is not critical. When the latter is the case, the above amides are excellent multifunctional lubricants in flexible film and sheet. Stearamide is used mainly in filled applications, oleamide in clear or translucent sheet. Although it is feasible to formulate stabilizer systems that overcome effects on heat stability, there has been a trend towards replacement with ester lubricants.

A special class consists of amides that have been converted to alkoxy derivatives. They are external in PVC, because partial neutralization of the high polarity of the amide group. At the surface, the alkoxylated amide group attracts atmospheric moisture, forming a two-dimensional surface network with strong hydrogen bonding. This can reduce the surface electrical resistivity of the compound by orders of magnitude, allowing static charge to drain readily. When using nitrogen-containing antistatic agents in PVC, it should be recognized that, in some cases, heat stability may suffer. In others, however, they may be used without ill effect (i.e., where there is not strong stabilizer demand). Antistatic agents are discussed more fully in the following.

The most important amide lubricant used in PVC compounding is ethylene bis-stearamide (EBS). In dilute solution, this diamide is internally hydrogen-bonded, satisfying the polar functional groups. As a result, EBS provides external lubrication, rather than the multifunctional behavior of stearamide or oleamide. EBS will, however, form complexes with carboxylic acids, carboxylate salts, and other polar additives. For instance, a one-to-one complex is formed with calcium stearate, resulting in a multifunctional lubricant. In actual practice, EBS is most often used in concert with either an internal or a multifunctional lubricant. The most common applications are rigid siding, profiles, and molded fittings, with EBS being used (usually) with calcium stearate. The combination tends to provide much processing latitude; in service, EBS then functions as a slip agent without giving evidence of an oily or waxy surface. In phonograph records, the EBS complex with barium or lead stearate is used in an analogous manner. Rigid film and sheet, where clarity is a factor necessitating minimum metal content, combinations of EBS with internal ester lubricants are used.

12.2.5 Esters

The behavior of ester lubricants in PVC is complex. In unplasticized PVC, long-chain esters, such as stearyl stearate and distearyl phthalate, are primarily external and, other things being equal, retard fusion time. They are used with or, at times, in place of EBS, in siding, profiles, and molded fittings. Such use is common in instances where sufficient process safety or output is difficult to achieve with less expensive paraffin wax/calcium stearate combinations. It is often useful to adjust fusion time with paraffin and calcium stearate levels and then improve processing with processing aids or combinations of the latter with ester lubricants. This will be considered further under specific applications.

Short-chain esters such as butyl stearate are, on the other hand, internal in rigid PVC. They may be used at trace levels to improve penetration of calcium stearate into the resin granule. Intermediate-chain-length esters (e.g., isooctyl stearate) appear to be multifunctional in unplasticized PVC, and can serve in combination with more complex ester lubricants. In plasticized PVC compounds, particularly those with polar plasticizers (e.g., relatively short-chain phthalates) all of the above simple esters are mainly external. Combinations with low-MW PE provide good release without bleed or exudation.

In rigid PVC, glyceryl monostearate (GMS) is multifunctional. The major usage is in bottles and film and sheet. Combinations of GMS and organotin stabilizers provide high clarity. GMS is also used in opaque, lead-stabilized rigid compounds, contributes to heat stability, and is relatively low cost. The glyceryl monoester of 12-hydroxystearic acid, although more expensive, is also used in unfilled compounds and may provide higher clarity. Glyceryl tris(12-hydroxystearate) can be added to increase resistance of clear compounds to water blush. Glyceryl monooleate has higher plasticizer compatibility than the stearate esters. It is used in fog-resistant clear semirigid packaging film. A further use is as a lubricant in mixed metal stabilizers for plasticized compounds.

Ester lubricants are based frequently on pentaerythritol. The mixed mono- and distearate ester blend is particularly useful in wire and cable compounds for improving output and providing a smooth surface without bloom. It is often used in combination with low-MW PE wax in high-speed extrusions. Some use has also been made in rigid PVC profile extrusions, for similar reasons. The latter application has also seen use of pentaerythritol tetrastearate, a lubricant of somewhat lower cost than the mono/diblend. The tetrastearate is, however, more external in rigid PVC and thus more prone to bloom or deposit.

When mixed esters of polyols are prepared using, in part, a dibasic acid, the product is an ester lubricant that is a low polymer. This leads to a high order of resistance to extraction, bloom, or deposition. Pentaerythritol adipate–stearate is used in clear rigid PVC compounds as an efficient multifunctional lubricant, despite its relatively high cost. The corresponding adipate–oleate, a liquid, is more generally used in plasticized compounds in conjunction with mixed metal stabilizers, particularly if the latter are relatively nonlubricating.

Waxlike ester lubricants are synthesized by esterification of montanic acid. A typical product is ethylene dimontanate, generally referred to as *montanic acid ester*. In the United States, this lubricant is used mainly in clear rigid PVC in high-end applications, in competition with pentaerythritol adipate–stearate. In these uses, it is known for high resistance to plateout. In Western Europe, products of this type are common in both rigid and plasticized PVC compounds for injection molding. The polymeric waxy ester may also be partially converted to its calcium salt, and is referred to as *partially saponified montan ester*. The metal content does not hinder clarity at the levels used (well below 1 phr), and the main use is as a multifunctional lubricant in clear rigid compounds.

12.2.6 Carboxylate Salts

In rigid PVC, the metal carboxylate used most often is calcium stearate. Its primary function is that of a fusion promoter. Although typically listed as an internal lubricant, in itself, it has little effect on compound viscosity. It is, on the other hand, a good surface treatment for calcium carbonate and may lower the process viscosity of calcium carbonate-filled compounds, particularly with untreated grades of filler. Calcium stearate also serves as a secondary stabilizer, and the two functions cannot be separated for compounding purposes. In phonograph record compounds, and occasionally in others, barium stearate is used instead. In lead-stabilized compounds, normal lead stearate ($PbSt_2$) is an excellent external lubricant. It also functions as a primary stabilizer, but is seldom used alone because of its low efficiency. Lead stearate should not be used as an internal lubricant in tin mercaptide-stabilized PVC unless the compound is black, as lead sulfide will be generated. Partly saponified montan ester can be used in place of calcium stearate (at higher cost). At times, blends are used (e.g., in compounds for injection molding). In such cases, the formulator is seeking a multifunctional, rather than an internal, lubricant.

Combinations of calcium stearate and paraffin wax in rigid PVC, without further lubricant addition, are generally not multifunctional.[11] Calcium stearate is added early in the mixing cycle so as to coat the resin grains. This promotes rapid fusion and an initial high process viscosity, useful in dispersion of fillers and pigments. It is this observation that has led technologists to reject the notion of calcium stearate being an internal lubricant, but rather to consider it as an external adhesion promoter for the resin grain. After fusion, the stabilizer–lubricant system complex is the actual internal lubricant.

Paraffin wax is usually added late in the batch to avoid coating the resin grains. The relative level versus that of calcium stearate governs the rate of fusion of a specific PVC resin. Resin selection also plays a part. If paraffin wax and calcium stearate are added simultaneously, or if a multifunctional lubricant is included, then internal versus external behavior are difficult to distinguish.[12] Both situations have their uses, to be discussed in connection with specific applications.

Plasticized PVC compounds using mixed metal powder stabilizers are frequently based on calcium or barium stearate or laurate. In the presence of plasticizer, such stabilizers typically act as multifunctional lubricants. Liquid stabilizers often use analogous salts of liquid acids, such as those of octoic, oleic, or tall oil acids. These are similarly multifunctional, as are combinations with organotin stabilizers. In many cases, mixed metal stabilizers provide sufficient lubrication such that no further lubricants are needed. This must be considered in replacement of nonlubricating lead stabilizer systems.

12.3 LUBRICANT SELECTION

In order to select a lubricant, it is necessary to consider the polarity of both the more polar and the less polar sections of the polymer; the same applies with respect to the lubricant; and to the process envisioned, as well as to the modifications of flow behavior desired. The fact that one is dealing with both polar and nonpolar interactions suggests the use of donor–acceptor scales as more or less quantitative measures. Although clearly a first-order approximation, the only such scale for which sufficient data exists is the comparison of solubility parameters. This is a first approximation because it considers the interactive behavior of two groups that may contact each other in a general sense, with no allowance for specific pathways by which reaction might occur. The approximation, therefore, reflects neglect of entropy terms. (This is very often what a first approximation does; the cancellation of such terms often occurs.) The solubility parameters of polar and nonpolar sections of polymers and lubricants may be calculated, among other methods, from functional group contributions to the heat of vaporization and the molar volume.[12] Compilations from a number of methods are given by Barton.[13]

12.3.1 Solubility Parameters in Lubricant Selection

For internal lubrication to predominate, the solubility parameter of the lubricant should be one to several $\mathrm{MPa}^{1/2}$ lower than that of the polymer. In the case of PVC, this implies a lubricant solubility parameter of 16–18. This condition is necessary, but not sufficient. In addition, the solubility parameter of the polar part of the lubricant should match that of the —CHCl— linkage, believed to be in the range of 19.5–20.[7] This match is provided by ester and carboxylate anion groups, and also by amide and carboxylic acid groups (when these are not internally hydrogen-bonded, reducing their polarity). The solubility parameter of the nonpolar part of the lubricant should be several units lower than that of the —CH_2— linkage in PVC (16.5–17). This relation is most often provided by alkyl side chains. Note that if the solubility parameter of the nonpolar part of the lubricant is increased (e.g., by adding polar groups) as it approaches the range of 16–17, the lubricant becomes a plasticizer.

If, on the other hand, predominantly external function is desired, the lubricant should be chosen so that its polar part is 1–2 $\mathrm{MPa}^{1/2}$ lower than that of —CHCl—, and its nonpolar section similarly lower than that of —CH_2—. The polar section may be an oxidized end group in a paraffin or PE wax, or even a branch point; the nonpolar section may again be a hydrocarbon side chain. The characteristic most often providing the difference between internal or external behavior in PVC is, therefore, the nature of the polar part of the lubricant. Multifunctional behavior results from broadening the solubility parameter of the polar group by using more than one type, and by using polar sites that vary in environment, such as the —OH groups in monoglyceryl esters. A multifunctional lubricant for PVC will usually contain polar groups having a solubility parameter covering the 16–20 range.

To be a filler surface treatment, the polar part of the lubricant should have a higher solubility parameter than the polar part of the polymer (note that this does not consider the occasional filler having a low energy surface, e.g., graphite). This permits the very polar filler surface, often $30-40\,\mathrm{MPa}^{1/2}$, to compete effectively with the polar sections of the polymer. With a polymer as polar as PVC, this becomes a difficult requirement. It is usually preferable, therefore, to pretreat the filler prior to mixing. Consideration should be given to actually bonding chemically to the filler surface. This is almost always sought when filler treatments other than lubricants are used (e.g., reactive silanes, titanates, or zirconates). With acidic fillers such as silica, when lubricants rather than reactive coupling agents are used, treatment of the filler with long-chain alcohols (e.g., polyethylene glycol) is preferred to use of amines or alkanolamines (e.g., triethanolamine), which can act as destabilizers in PVC. With salt-like fillers such as carbonates and silicates, stearates having the same cation (calcium stearate for calcium carbonate, magnesium stearate for magnesium silicate) are effective surface treatments. The simple measure of choosing the same cation permits the greatest extent of ionic bonding.

At low filler loadings, it is often not possible to distinguish between the effects of internal lubrication and filler treatment. Filler active site concentration is not high enough to tie up internally acting additives. At very high filler loadings, filler surface lubrication is likely to be the most important processing goal. For example, in PVC compounds containing very high levels of calcium carbonate (e.g., vinyl composition tile or cove base), calcium stearate has the primary function of improving flow in the vicinity of the calcium carbonate surface. The use level should probably be specified in parts per 100 of filler.

In applications involving filler treatment, two additional compounding cautions apply: lubricants chosen for other purposes (e.g., an external lubricant) should not contain filler-reactive groups. In addition, such additives should not interfere with filler treatment by complexing the reactant intended for the filler surface. Instead of circumventing such problems by separate filler pretreatment, they may often be avoided by judicious choice of point of addition of ingredients—that is, the filler treatment with the filler, and the internal lubricant with the resin. Mixing procedure cannot, however, compensate for every overextension of compounding latitude. For example, if stearic acid, normally multifunctional in PVC/VAc or EVA-PVC/VAc blends, were added to such a composition also containing magnesium hydroxide, perhaps as a flame retardant, it would bond to the filler regardless of the mode of addition, forming magnesium stearate.

The balance of internal versus external lubrication is particularly subject to change with changes in other ingredients in rigid PVC compounds. For example, the replacement of tin mercaptide stabilizer in pipe compounds with the same weight of antimony mercaptide shifts the overall balance towards internal lubrication. As a result, such substitution is generally accompanied by an increase in paraffin wax as external lubricant and a decrease in the level of calcium stearate used.

12.3.2 Lubricants in Processing

In high-shear mixing of pelletized compound, with either an internal batch mixer or a twin-screw extruder, the polymer flow characteristics desired are rapid wetting of particulates, high flow in their vicinity, and rapid self-wetting (recombination) during shear. In other words, it is desired that the steps of incorporation and distribution proceed as rapidly as possible, with an acceptable level (usually very low) of polymer degradation from shear and heat. This calls for internal lubrication and filler surface treatment at an early stage. In preparation of rigid pelletized compounds by such methods, internal or multifunctional lubricants are, therefore, added with the resin. With flexible PVC compounds, internal or multifunctional lubricants are usually added with the plasticizer, depending on the wetting action of the latter to carry the additive into the resin granule.

Some external lubrication may be required for clean exit of the mixed compound from the internal mixer or deposit-free production via twin-screw extruder. The point of addition of external lubricant is normally timed to occur after dispersion of particulates is complete, when using an internal batch mixer. With continuous extruder mixing of pelletized compound, it is preferable to rely instead on multifunctional lubricants. An important point to note is that as temperature and shear increase, partly compatible additives become less compatible with high polymers. A multifunctional lubricant that acted largely internally at the start of the extrusion process can, in consequence, become external at the head and die. With internal batch mixers, on the other hand, the end of the cycle is accompanied by higher batch temperatures but typically lower shear rates. Multifunctional action is, therefore, less certain. In actual practice, both use of multifunctional lubricants and separate early addition of internal lubricant with late addition of external are found. Often, this is a matter of practicality and convenience. It is common enough for the internal batch mixer to be fed from a ribbon blender containing a preblend of the entire batch, with no provision for multiple additions (this, of course, defeats the major advantage of the internal batch mixer—its versatility). Modifications to a piece of equipment, such as to a batch mixer in an attempt to duplicate a continuous mixer, are best installed so as to be easily reversible.

Most rigid and much flexible PVC is, however, not processed into pelletized compound. The bulk of rigid PVC is mixed and fabricated in one step from dry blends. In this process, final mixing and fusion of the compound may occur essentially simultaneously with shaping, as in extrusion, or just ahead, as in calendering and injection molding. The nature of the fabricating process bears strongly on lubricant selection. In extrusion from dry blend, the compressed time scale between mixing and shaping militates against the use of multifunctional lubricants in cases where a lubricant must function first internally, then externally. There is not sufficient time. Pipe and conduit extrusions typically use calcium stearate as internal lubricant and paraffin or other wax as external. In the dry blending step, calcium stearate is added with the resin to promote fusion, and wax later in the cycle. The well-mixed dry blend contains PVC granules with lubricant and stabilizer associated with its internal fine structure. Internal lubricant may also be associated with the fillers and pigments used in such compositions. This picture is consistent with rapid fusion; measures to control fusion will be discussed with examples in the following.

As the time interval between mixing and shaping is increased, opportunity for multifunctional behavior also increases. The examples dealing with calendering and molding of unplasticized compounds (Section 12.4) cover a number of multifunctional lubricant combinations.

Flexible PVC is also fabricated from dry blend rather than fluxed compound. Internal and multifunctional lubricants are normally added with the plasticizer. Purely external lubricants such as paraffin and EBS wax are used, but most often are added with the plasticizer and stabilizer, leading to complexing and multifunctional behavior. In some plasticized PVC compounds, external lubrication is obtained by use of multifunctional lubricants. The wide variety of applications for flexible PVC has led to a high degree of customizing of lubricant systems, often in conjunction with stabilizers developed for specific uses.

12.4 EXAMPLES OF LUBRICANT SELECTION

This section describes prevalent practice in the United States, with some reference to alternative systems used in Western Europe. The effects on end product performance when less than optimum choice of lubricant and lubricant level is made are also considered.

12.4.1 Rigid PVC Pipe and Conduit

When using tin "reverse ester" mercaptide stabilizers in dry-blend compound for twin-screw pipe extruders, the most prevalent usage for pressure pipe used in water delivery centers around 0.4–0.8 phr calcium stearate as internal lubricant and 0.8–1.0 phr of paraffin wax as external lubricant. Often 0.1–0.2 phr of oxidized PE wax is added; this confers a certain degree of multifunctionality to the package.

PRESSURE PIPE

PVC	100
Calcium stearate	0.4–0.8
Paraffin wax	0.8–1.0
OPE	0.1–0.2

(other ingredients omitted)

The combination promotes rapid fusion and high output, without leading to a surface difficult to print. None of these lubricants forms an effective PVC plasticizer. As a result, the heat distortion temperature and mechanical properties of the polymer are essentially unaffected. In rigid PVC compounds, the use of less than 1.0 phr internal lubricant generally lowers the glass transition temperature by less than 5 °C. The relatively low-energy surface provided by paraffin and OPE wax, although printable, contributes to good abrasion resistance. These additives have good service stability, are nontoxic, and are low in taste and odor. If pipe is run from a single-screw extruder, longer dwell and lower output will be found. Calcium stearate here is used at a level of 0.75–1.5 phr, with paraffin wax at 0.5–0.75 phr. With this higher overall level of lubricant, oxidized waxes are not generally used. Excessive use of external lubricants must be avoided to avoid deposition. In addition to generating surface imperfections, deposits tend to dissolve resin, which eventually decomposes with interruption of output.

Lead-stabilized pipes often use 0.3–0.4 phr of calcium stearate as internal lubricant, 0.15–0.3 phr of paraffin or Fischer–Tropsch wax as external lubricant, and 0.8–1.2 phr of blends of normal lead stearate and dibasic lead stearate as the stabilizer/lubricant combination. In addition, 0.1–0.3 phr of stearic acid is also common. These combinations are believed to be effective in generating high output with reduced extruder wear, but appear to be linked strongly to the use of lead stabilizers.

Conduit formulations, because of their higher filler loadings, and because they are often run on single-screw extruders, use a higher overall lubricant content. Levels of calcium stearate in the range of 1.0–1.5 phr and paraffin wax at about 1.0 phr are common. The increase in calcium stearate usage with increasing filler content is typical, and reflects a greater need for flow in the vicinity of filler particles. In many cases, the filler is calcium carbonate pretreated with a surface layer of calcium stearate. The latter contributes to overall lubrication, but should not be thought of as available as a secondary stabilizer. The increased level of lubricant results in measurable decrease in glass transition temperature, with consequent loss of flexural stiffness and resistance to distortion. In this application, these effects are not serious.

Drain, waste, and vent (DWV) pipes are other examples where filler loadings exceed that of pressurized pipe. Calcium stearate is commonly used at a level of 0.6–0.8 phr, with paraffin wax at 1.2–1.5 phr. In these applications, a further 0.1–0.2 phr of OPE is also common. This tends to preserve printability even in filled compositions requiring substantial external lubrication.

DWV PIPE

PVC	100
Calcium stearate	0.6–0.8
Paraffin wax	1.2–1.5
OPE	0.1–0.2

The development of foam core pipe has introduced a new variable. In the foam layer, fusion must be synchronized with foam cell development so as to produce a uniform closed cell structure. This requirement tends to fix the levels of calcium stearate and paraffin. The consequence is that, instead of additional lubricants, processing aids are used.

FOAM CORE PIPE

PVC	100
Calcium stearate	0.6–0.8
Paraffin	0.8–1.0
Processing aid	2–4

12.4.2 Molded Products

Molded pipe fittings—the largest application for injection molding of rigid PVC—are illustrative of many other applications: during mixing and fusion in the extruder section of the press, strong internal lubrication is needed to moderate shear stress. Subsequent to this point, as flow is required in runners, through gates, and in filling mold cavities, combination internal and external lubrication is needed. In injection molding, the polymer molecules must continue to flow with respect to each other well after the extruder section has been left, rather than flow only in relation to metal surfaces, as in exiting a pipe extruder. In tin-stabilized pipe fittings, 1.0–1.5 phr calcium stearate is used with paraffin wax and in some cases with processing aids.

PIPE FITTINGS

PVC	100
Calcium stearate	1–1.5
Paraffin wax	1–1.5
Processing aid	0–1.5

Sometimes, a multifunctional ester such as a pentaerythritol mono/distearate blend is added. The latter has sufficient polymer compatibility to be highly bloom-resistant, even at these levels. In molded articles, shape complexity requires enhanced release; about 0.1 phr of EBS may be added.

Lead-stabilized fittings generally use higher overall lubricant levels. Calcium stearate may be increased to 1.5–2.0 phr with the other lubricants held as above. In some cases, calcium stearate is left at 0.75–1.0 phr, and multifunctional ester lubricant increased. Deciding on a compounding direction hinges on whether the particular situation seems to call for greater compound flow in itself, or a combination of lower viscosity plus enhanced flow in the region of metal surfaces. Note that this decision cannot be separated from considerations of mold design, runner size, gate diameter, and the like. What appear as divergent solutions to the same formulating problem may reflect very different details of process.

Molded parts of complex configuration often employ lubrication systems similar to the above—not so much from the need for very high output, but in order to enable sufficient flow.

LIGHT DIFFUSER PANEL

PVC	100
Calcium stearate	0.8–1.2
Paraffin	0.8–1.2
Processing aid	2–3
Lubricating processing aid	0–1

12.4.3 Extrusions for Outdoor Service

Compared with extruded pipe and conduit, rigid PVC extrusions for outdoor use (e.g., siding and profiles for window components) are similar in that high output is required, but differ in many other characteristics. Close dimensional control in thin cross-sections involves accommodating high shear rates. Taken with the need for excellent surface characteristics, the process calls for multifunctional lubrication. Conditions of service require high resistance to UV light in the top layer, referred to as the capstock, and the underlying composition, the substrate.

SIDING SUBSTRATE

PVC	100
Calcium stearate	1–1.2
Paraffin	1–1.3
OPE	0.1–0.2

Although vinyl siding is extruded as a simple sheet, it is then thermoformed to the actual siding configuration, in line with extrusion; that is, at high speed. The process requires a high lubricant content. This is even more the case with the capstock layer, where high output is combined with the need for a perfect surface.

SIDING CAPSTOCK

PVC	100
Calcium stearate	1–1.5
Paraffin	1–1.5
Processing aid	0.2–1

In foam layers for vinyl siding and in foamed sheet generally, synchronization of cell development and fusion limits lubricant content, and higher levels of processing aids are used.

FOAM SHEET

PVC	100
Calcium stearate	0.3–0.5
Paraffin	0.6–1.0
Processing aid(s)	4–6

Similar considerations affect the additive systems used for foamed PVC–wood fiber composites. In these, ingredients specifically for the wood fiber (e.g., biocides, tannin stain inhibitors, and coupling agents) are best coated on the fiber prior to incorporation in the compound.

WOOD COMPOSITE

PVC	100
Calcium stearate	0.6–1.2
Paraffin	1–1.2
Processing aid	2–6
Lubricating processing aid	0–1

Outdoor profile extrusions, typically for window components, are also run at high speed and use complex processing systems.

PROFILE EXTRUSION

PVC	100
Calcium stearate	0.8–1.2
Paraffin	0.8–1.2
Processing aid	0.7–1.0
Lubricating processing aid	0–0.2

Lead-stabilized products, used in some parts of the world in rigid extrusions, often contain 0.4–0.8 phr of calcium stearate as internal lubricant, 0.2–0.5 phr of stearyl alcohol to improve the mobility of the stabilizer (normally dibasic lead phosphate or combinations with tribasic lead sulfate), and 0.4–0.75 phr of partly saponified montanic ester as a multifunctional lubricant. For the ultimate in process stability, calcium stearate may be replaced by a barium/cadmium stearate blend. The inclusion of cadmium also reduces the severity of staining by airborne sulfur compounds. Although lead-stabilized rigid compounds offer advantages in material cost and process safety, their use should be abandoned because of the hazard involved and because such usage is prejudicial to acceptance of vinyl products.

12.4.4 Rigid Film and Sheet

Pigmented printable film and sheet using tin stabilization generally employ 0.5–1.0 phr calcium stearate as internal lubricant. External lubrication is provided by 0.1–0.3 phr of oxidized PE wax, or, in some cases, by 0.1 phr EBS. The rest of the lubricant package is usually 0.3–0.5 phr of a multifunctional lubricant such as montanic acid ester or glyceryl 12-hydroxystearate. This combination forms an interacted package that is resistant to plateout on calender rolls and that does not interfere with printing and decoration. In general, resistance to plateout correlates with printability. Stearic acid should be avoided as well as wax. Rigid and semirigid sheet not intended for printing or decoration use lubricant systems as described above for siding components.

Clear film and sheet tend to use 0–0.5 phr calcium stearate, with greater reliance on multifunctional lubricants.

CLEAR RIGID SHEET

PVC	100
Processing aid	1.5–2
Lubricating processing aid	0.4–1
Ester lubricant	1.2–1.5

External lubrication generally uses on 0.1–0.3 phr of oxidized PE wax in cases where printing or decorating is contemplated, or 0.1 phr of EBS if slip characteristics are desired. The remainder of the lubricant system is multifunctional, using the esters given above or GMS, in some extruded sheet, at levels of 0.3–0.5 phr. In applications where the greatest clarity is required, the GMS is often replaced with glyceryl dioleate or pentaerythritol adipate oleate. These avoid the slight haze that may result from side-chain crystallization of saturated alkyl groups, and are also used in blown rigid film. Unsaturated esters (e.g., oleates) are normally detrimental to heat aging. The use of tin mercaptide stabilizers compensates for this in this application. Semicrystalline external lubricants such as paraffin or PE wax may be used at trace levels (<0.1 phr) without resulting in objectionable haze, but are rarely of value in the systems discussed above.

12.4.5 PVC Bottles

Transparent rigid PVC containers are usually tin-stabilized. External lubrication is provided by OPE wax at levels of 0.1–0.3 phr, preserving a surface capable of printing or decoration. In this application, two high-shear processes—mixing of pelletized compound and injection molding—must be accommodated. The remainder of the lubricant system therefore uses a relatively high level (0.7–1.0 phr) of multifunctional lubricant, often a blend of GMS and montanic acid ester. If the greatest clarity is desired, glyceryl esters of 12-hydroxystearic acid and pentaerythritol adipate–oleate replace the former esters at somewhat higher cost.

Containers stabilized with nontoxic calcium/zinc powders are popular in applications where opacity or translucency is acceptable. (Here “nontoxic” is used in a commercial sense, denoting a low order, not absence, of toxicity.) In these cases, the stabilizer, used at a level of 1.0–1.5 phr, serves as internal lubricant. External lubrication is provided by OPE wax as above. The remainder of the lubricant system is often 0.5–1.0 phr GMS or blends of GMS with montanic acid esters.

12.4.6 Flexible Film and Sheet

Flexible PVC film and sheet are now typically stabilized with barium/zinc and calcium/zinc liquids at levels of 2–3 phr. With plasticizer levels of 20–60 phr, the components of the liquid stabilizer also serve as multifunctional lubricants. This is often supplemented with 0.1–0.3 phr of stearic acid, particularly when high-efficiency liquids, used at 0.8–1.5 phr, replace standard liquid stabilizers. In some instances, the liquid stabilizer is supplemented with a powder booster, usually a mixed metal stearate or laurate. In these cases, further need for multifunctional lubricant is rare. Where slip characteristics are desired, 0.3–0.8 phr of EBS are commonly added. Calcium stearate is often added if untreated calcium carbonate is used as a filler, generally at about 0.5 part per 25 phr filler. It is best to add this with the filler for direct adsorption. Injudicious use of calcium stearate can affect an otherwise optimum ratio of metals in a mixed metal stabilizer system. Stearic acid, the most popular lubricant used in flexible PVC, must be used with great caution so as not to cause plateout or interfere with printing or finishing. The use of 12-hydroxystearic acid is preferable. Another feature that tends to correlate with low plateout and good printability is ease in heat sealing operations.

Tin-stabilized semirigid sheet is generally treated comparably to rigid compounds, with 0.3–0.5 phr of calcium stearate for internal lubrication, and 0.75–1.0 phr of a blend of paraffin wax and OPE wax for external lubrication. When stabilized instead with mixed metal powders, usually as a paste in epoxidized soybean oil, further lubricant addition is not often required.

12.4.7 Wire and Cable

Lead-stabilized wire coverings generally use 0.2–0.5 phr of stearic acid to increase the mobility of the stabilizer; that is, to act as an internal lubricant in the vicinity of the insoluble stabilizer particle. If the stabilizer itself is soluble, as with barium/lead stearate blends, the addition of stearic acid is unnecessary. The practice of using 0.25 phr stearic acid has carried over to those compounds that use barium/zinc or calcium/zinc stabilizers, where it is also probably unnecessary.

It is axiomatic that PVC wire coverings must be processed at very high output. In cases where material cost is a dominating factor (e.g., building wire and automotive primary wire), reliance on stearic acid continues. Communications wire has, on the other hand, gained in output while maintaining the high appearance standards by use of multifunctional lubricants such as pentaerythritol mono- and distearate blends. At levels of 0.2–0.5 phr, excellent processing is obtained with complex color-striped extrusions at high speeds, without the die plateout or bleed that can occur with stearic acid. Glycerol analogs (e.g., GMS) are generally avoided in lead-stabilized flexible compounds, as dehydration assisted by the stabilizer can produce unsaturated residues, leading to discoloration. Pentaerythritol-based mono- and diesters are not subject to dehydration under normal conditions because of the absence of hydrogen on the carbon atom adjacent to the C—OH group.

PVC jackets and insulations for unjacketed constructions that are printed often contain 0.1–0.3 phr of OPE wax. It is feasible, however, to print such constructions without this additive through judicious choice of ink. When OPE wax is used, and stearic acid content reduced or eliminated, the surface is more readily wet by the nylon coating that is dual-extruded over building wires such as Underwriters Laboratories Type THHN. This permits higher line speeds, with a lower incidence of rejection.

12.4.8 Further Applications in Flexible PVC

Lubricants are used extensively in rigid PVC because few products could be fabricated without such use, or could be fabricated only at output low enough to ensure displacement by competitive materials. Lubrication began with the use of stearic acid with lead stabilizers, and with calcium stearate–paraffin wax blends with other stabilizers. In rigid PVC compounding, it has progressed from this point as processing has become more complex. (It should be noted, however, that stearic acid remains the most prevalent lubricant used with lead stabilizers, and calcium stearate–paraffin wax blends persist as the largest-volume lubricants in overall use.)

Many plasticized PVC articles can be fabricated without the addition of lubricants, because plasticization enables sufficient flow and because, in the presence of sufficient plasticizer, otherwise internally acting stabilizers become multifunctional lubricants. The examples (given in the sections dealing with flexible PVC) are directed, for the most part, at cases where a lubricant is added to enhance the properties or to improve the output of an otherwise satisfactory product. This may be extended to several categories that cross product lines: one such comprises highly filled flexible PVC. The major applications are floor tile, cove base, and roofing membrane. These applications involve processes whose output depends on achieving flow despite large quantities of filler particles. It is generally not economically feasible to use pretreated fillers in these cases. Practice has largely switched from stearic acid (0.5–1.5 phr) to calcium stearate (0.2–0.5 phr) as combination internal lubricant and filler treatment. Future developments might include blends of calcium stearate with multifunctional ester lubricants to improve output without exudation, and experimentation with oxidized waxes for surface characteristic modification.

12.5 RELEASE AND SLIP AGENTS

The same additive that provides external lubrication, also for example, enables rapid filling of mold cavities, and is likely to assist mold opening and clean ejection of molded parts. In a similar manner, the external lubricant, after improving output in extrusion, is likely to assist in preventing self-adhesion of extruded film and sheet. In the first case, the additive is then thought of as a release agent; in the second, as a slip additive. In both cases, the external lubricant may also be contributing antistatic characteristics. (Additives, such as filler particles, that limit adhesion of wound layers of film or sheet by decreasing the extent of surface contact rather than by lowering surface energy are usually referred to as antiblocking.)

The most common release agent used in vinyl compounds, when the lubricant system is not in itself adequate, is EBS, typically at 0.05–0.2 phr. If the article is to be printed or decorated, it is preferable to use a blend of GMS and OPE, both at 0.05–0.1 phr. The most widely used slip agent in rigid vinyl is stearamide, whereas in flexible compounds, oleamide, is used, both at 0.05–0.2 phr. The use of fluorinated die release agents has not been widely investigated as regards PVC extrusions, but—based on their effects in polyolefins–should be. Systems based on tetrafluoroethylene (TFE) oligomers are available from 3M (Dynamar®), DuPont (DryFilm®), Daikin (Polyflon®), and (based on hexafluoropropylene oxide, PFPE) from Solvay Solexis (Fomblin®).

12.6 ANTISTATIC AGENTS

Antistatic agents are additives used to reduce the tendency of polymeric compositions to acquire or maintain a surface charge. The problems that surface charge may cause range from dust pickup by phonograph records or tapes to spark discharges to or from plastic articles. The consequences of a spark discharge can be disastrous in environments containing combustible dust (e.g., mine conveyor belts) or high oxygen levels (e.g., operating rooms and other hospital locations). The voltage potential associated with electrostatic charge can destroy the encoding of information in computer storage devices and can interfere with electronic communication. Another associated effect, found typically with plasticized PVC film and sheet, is condensation of moisture into microdroplets that do not merge and run off, but persist as surface fog. This effect, known as "water fogging," should not be confused with fogging referring to the condensation of volatile ingredients from the compound onto other surfaces, such as automobile windshields.

Electrostatic charge is a surface phenomenon involving either a deficiency or an excess of electrons on an ungrounded insulator. It is most often generated on plastic surfaces through frictional contact with a second plastic surface, a moving fluid (even air), or the surfaces of processing equipment. Every process step that generates new surfaces will produce (or alter) electrostatic charge. This includes not only processes that obviously generate new surfaces, such as milling, calendering, or extrusion, but also less obvious steps, such as mold opening. Further handling of the finished article—part tumbling, or conveying of film or sheet, even movement during transport—can produce surface charge. In such operations, if there is any chance of spark discharge occurring, external antistatic devices are used in addition to additives present in the compound.

Static charge can decay by several mechanisms. The most obvious—a spark discharge—is generally intolerable. Alternatively, the energy of the electrostatic field may be converted to kinetic energy: the charged plastic article may move. This often interferes with film, sheet, and fiber handling. The static charge may also be lost to ambient air—usefully if transferred to molecules of water vapor, less so if neutralized by charged incident airborne dust particles. Finally, the charge may drain off along the surface of the plastic to ground. Some charge will also be lost through background radiation by charged particles, but this occurs too slowly to be valuable in practice. Antistatic agents function by promoting the loss of electrostatic charge through useful mechanisms (surface conduction or transfer to atmospheric water vapor). It should be emphasized that all electrostatic fields (not in vacuum) will decay and that, if an acceptable decay path is not provided, an unacceptable one will result.

Although there may be some overlap in individual cases, compounding to minimize electrostatic discharge (ESD) is distinct from that used to provide protection from electromagnetic (EMI) or radiofrequency interference (RFI). In the latter cases, compounds use conducting fillers (or polymers) to provide an overall volume resistivity in the range of 10^3-10^6 ohm cm (volume resistivity (VR) is the resistance of a unit volume of the composition). It is also known as the specific insulation resistance. It is calculated as $\mathrm{VR} = RA/T$, where R is the resistance, A is the cross-sectional area, and T is the thickness or length of the specimen. Thus, when R is measured in ohms, A in cm^2, and T in cm, VR is measured in ohms $\mathrm{cm}^2/\mathrm{cm}$, or ohm cm, it should be noted that, in terms of actual physical properties, the units are ohms, measured under certain dimensional constraints. The concept of resistance times length is here merely a construct, not a fundamental property. For example, a 10 cm length of a composition having a volume resistivity of 10 ohm cm, will yield a reading of 100 ohm on a test device only if it has a average cross-sectional area of 1 cm^2. Compositions having volume resistivities in the range of $10-10^6$ ohm cm are typically referred to in industry as "semiconducting," although they are classified by the Department of Defense as "electrically conductive."[14]

Most commonly, 15–35 weight percent of a semiconducting thermoplastic composition will consist of EC (electrically conducting) or XCF (extraconducting) furnace process carbon black. Incident electromagnetic radiation, radiofrequency or otherwise, is dissipated in the form of small but measurable leakage currents to ground. This leakage current is presumed to travel throughout the composition, although, as with metallic conductors, it is probably concentrated towards the surface. Electronic conduction occurs within the filler particle, generating an electric field that induces a similar current in a closely adjacent particle. Increasing kinetic energy tends to interfere with this orderly process (as with electronic conduction generally). Therefore, the volume resistivity of typical semiconducting plastics increases with temperature; that is, they become less conductive. In contrast, when conduction involves movement of ions, as can occur with drainage of electrostatic charge, the reverse is true, conduction increases with temperature. When both mechanisms operate, electronic conduction usually predominates.

Black-filled compositions will often, but not always, have ESD as well as RFI and EMI characteristics. A black-filled PVC phonograph record, for example, will block electromagnetic fields, but nonetheless will often be readily charged electrostatically if antistatic additives are not used. In cases such as this, the surface of the article invariably proves to be far less conducting than bulk properties would suggest.

ESD compounds can usually operate with much higher resistivities than those designed to defeat EMI or RFI. In most cases (some exceptions will be mentioned), a resistivity of 10^6-10^9 ohm is adequate. In the case of ESD, the resistivity in question is surface rather than volume. Surface resistivity is the resistance, in ohms, of a unit two-dimensional square centimeter of the surface of a composition. Formally, the dimensions are ohms per (length per width), ohm/(cm/cm), or ohm. The concept of a purely two-dimensional measurement is, however, clearly artificial. Surface resistivity is the volume resistivity that is observed using electrodes mounted on one surface, with the assumption that he surface carries all of the leakage current. Most literature references list surface resistivity in ohms, occasionally ohms/square. When clean surfaces are measured, the surface resistivities of most polymers are slightly lower (that is, the surfaces are more polar) than their volume resistivities because of unsatisfied valence forces at the surface. In practice, however, the surface of a composition may not reflect the volume resistivity of the bulk ingredients. For example, the volume resistivities of rigid PVC compounds (other than black-filled), not specifically compounded with antistatic agents, are in the range of $10^{11}-10^{14}$ ohm cm.[15] For some applications, the lower part of this range is adequate. If the actual surface is really paraffin wax lubricant, then the surface resistivity may be 10–100 times greater, effectively blocking charge dissipation. Use of antistatic additives, as outlined in the following sections, can decrease the resistivity of rigid PVC by factors of 100–1000, often eliminating static problems.

Flexible PVC compounds not containing antistatic agents have volume resistivities in the range of $10^{10}-10^{13}$ ohm cm, depending on overall polarity.[16] This, again, does not address the nature of the actual surface. If compounded with antistatic additives as described in the following sections, improvements of 2–4 orders of magnitude are possible, subject to the constraints that the lower the initial surface resistivity, the less additional decrease should be expected; and that the higher the level of antistat added, the more likely it is that side effects will occur.

12.6.1 Types of Antistats

Similar to the jargon used with release agents, antistats are considered to be internal if added to the compound and external if, instead, applied to the surface of the product. This is at odds with prevalent nomenclature regarding lubricants, where "internal" denotes internal action, "external" referring to surface lubrication by an agent that has previously been incorporated into the compound. In some cases, an external lubricant may be both an internal release agent and an internal antistat. The use of such nomenclature may be somewhat lacking in logic—but probably no more so than referring to PVC polymer as a "resin" (a legacy from times when the only commercial plastics were alkyd and phenolic resins).

External antistats are often extremely effective, lowering surface resistivity by increments of as high as $10^{6}-10^{8}$ ohm.[17] In general, their action is not permanent. The additives used commonly migrate into the compound, become contaminated with airborne dust, are rubbed off, or abraded away. Internal antistats, although usually not providing as great a decrease in surface resistivity, are considered permanent.

12.6.2 Mechanism of Internal Antistatic Function

Internal antistatic agents have one common characteristic: to be effective, they must come to the surface. Therefore they must have the characteristics associated with "external" lubricants. Once at the PVC surface, they may function by one or both of the following mechanisms:

- Decrease in the coefficient of friction of the surface
- Transfer of static charge to ground or to the atmosphere

Decrease in Coefficient of Surface Friction Here, the additive acts entirely as an external lubricant: friction during processing occurs between lubricant-coated PVC and lubricant-coated process surface, instead of between PVC and metal. The interaction is much weaker, with lower frictional development of charge. For this to occur, the antistat additive must be partly compatible with the polymer. That is, its solubility parameter must be lower than that of PVC (18–19 SI units) or plasticized PVC (usually 17–18 SI units), but not so low as to be incompatible (more than 3–4 SI units difference). Friction-reducing antistats, as with external lubricants, tend to contain both polar and nonpolar sections. For external action, the nonpolar part should have polarity similar to the nonpolar area in PVC (i.e., a hydrocarbon section). The polar part of the additive should be less polar than the carbon–chlorine bond in PVC, so as to permit migration to the surface (in competition with internal attraction to the polymer or to polar filler particles). If the polar section of the additive is chosen to be more polar than the polar part of the polymer, it will function primarily internally, as a filler treatment, internal lubricant, or both.

The use of external lubricants is attractive from other considerations: lubricants are generally inexpensive and bring other benefits such as increased output. In addition, their effects in service are usually well known. Most often, however, the level of external lubricant needed for antistatic purposes is greater than would be chosen based only on processing considerations. The consequences of overuse of external lubricants in PVC are rarely acceptable. There is, in addition, a further caution. The external lubricant that has lowered friction during processing, resulting in lower static charge development, may contribute to a more insulating surface afterwards. Particularly in PVC, paraffin or similar waxes (the most common external lubricants) can generate a surface resistivity as high as 10^{16} ohm. With polymers as polar as PVC, many of the static charge problems that arise after processing derive from nonpolar surface layers.

Transfer of Static Charge to Ground or Air Additives that are more traditionally considered antistatics act through an additional, more widely effective mechanism. After migrating to the surface, polar groups in the additive adsorb sufficient atmospheric moisture to form a surface monolayer that is essentially a two-dimensional aqueous solution. The polar groups of the additive must be well suited to the extensive hydrogen bonding needed to link together such a structure. The ionic strength of the surface layer tends to increase by attracting trace salts from the bulk of the compound, and, often more significantly, from airborne particles. (Although one may not think of ambient air as a source of ionic compounds, one need only uncover a beaker of extra low conductivity water in the laboratory and follow the decrease in measured resistance with time to become convinced.)

The surface layer develops to a greater or lesser extent the ability to conduct surface charge to ground, primarily by rapid proton transfer in the hydrogen-bonded surface network, secondarily by ionic transport, and by direct dissipation to the atmosphere. (High relative humidity (RH) can reverse the significance of these modes.) The magnitude of the surface current is too small to observe directly with ordinary laboratory instrumentation. Measurements are made, instead, of the decrease in intensity of electrostatic charge, or, more frequently, of the decrease in electric potential that the charge induces in test equipment. The rate of charge decrease, other things (e.g., RH) being equal, increases with increasing temperature, as would be predicted by either ionic dissipation or conduction. This is the reverse of the behavior of electronic conduction with temperature. In theory, combinations of conductive filler and antistat additives might be used to achieve more or less constant resistivity versus temperature. In practice, antistats, at least to date, have tended to interfere with filler conduction.

The aqueous surface is in equilibrium with the vapor pressure of water in the atmosphere. As a result, the effect of antistats is a function of relative humidity. No comparative data on effectiveness of antistatic additives is meaningful without reference to relative humidity. In addition, many additives that are effective at 50 percent or higher RH become useless at very low RH. It is very difficult to quantify the exact dependence of antistatic activity on relative humidity. The form of the equation relating dissipation of charge to moist air is known to be exponential. The relationship of charge transport properties of hydrated protons in hydrogen bonded surface networks to relative humidity can, however, only be guessed at.

The standard means for attempting to minimize RH dependence is to include polar groups of extremely high water affinity (so as to reduce the fugacity of water from the solution). Water absorption is not normally a property that the formulator seeks to maximize. Therefore, additive levels must be kept very low so that a surface monolayer is the only (or the major) effect. Levels of 0.05–0.2 phr are possible in some applications. At the lower end of this range, most antistatic additives prove relatively harmless to overall properties of PVC compounds (note that this assumes that there is no other vital additive that might complex or react with a particular antistat). At levels of 0.2 phr or greater in PVC, side effects bearing on release and printability are possible.

12.6.3 Types of Internal Antistats

In structure, antistats, not surprisingly, tend to resemble surfactants. They are thus subject to the same terminology: ionic or nonionic. Without comment on the bonding involved in media such as semipolar polymeric compositions, it may be safely assumed that an “ionic” antistat (or surfactant) would show some measure of ionic dissociation or conductivity if it were added to water, but that a “nonionic” analog would not. It should be noted that the behavior to be expected in media of much lower dielectric constant than water is far less black and white.

12.6.3.1 Nonionic Antistats

Esters The most common nonionic antistats used in PVC are esters of polyols, such as glycerol or sobitol, with aliphatic fatty acids. Polyol esters offer several advantages: nontoxic character, FDA sanction, ready biodegradability, relatively good heat and UV light stability, and modest cost. In most PVC compounds, polyol esters (e.g., GMS) function both as internal and external lubricants. In rigid PVC (film, sheet, and bottles), there is enough external function to decrease surface resistivity. At the levels needed (0.1–0.3 phr) for antistatic activity, applications requiring high clarity must avoid sidechains with crystallization tendencies (e.g., GMO rather than GMS). In flexible PVC, polyol esters are largely internal, particularly if highly plasticizer compatible. External behavior (and consequent antistatic action) can be made to predominate by inclusion of an externally active additive capable of coordination to the polyol ester. This can often be achieved by addition of 0.1–0.2 phr of EBS. The same approach can also be used in semirigid PVC compounds. Note that this use of one lubricant to externalize another depends on the overall balance of ingredients. If there is present a third additive with coordinating power that is strongly internal or markedly multifunctional (e.g., complex esters), this route may not work at all. The total additive complex may, in such cases, be internalized instead.

Phosphate partial esters of fatty alcohols (e.g., lauryl acid orthophosphate) form a class of nonionic antistats that, although useful in polyolefins, find little application in PVC compounding, being, in most cases, prodegradants.

Ethoxylated Amines A class of nonionics that does find use in PVC is that of ethoxylated tertiary amines of the structure $R—N(CH_2CH_2OH)_2$. In this general formula, R denotes a relatively long-chain alkyl group of incompatibility to drive the additive to the PVC surface. Surface adsorption of water again leads to a hydrogen-bonded network capable of draining off charge. The ethoxylated amine structure is particularly well adapted to chelate metal ions, thereby making this class of nonionic antistats more efficient in capturing ionic debris from the atmosphere than polyol esters. This gain in efficiency must be weighed against several other factors, including the fact that such additives also complex a range of other metals, for example, mixed-metal stabilizers. The result, in some but not in all cases, can be a reduction in heat stability.

Ethoxylated amines may be used at low levels, generally a maximum of 0.1 percent by weight of the composition, in food contact applications. Higher levels (necessary for more than slight improvement in antistatic character) can be used only in non-FDA sanctioned applications. At levels above 0.1 percent, some loss in heat stability (as with all amine additives) is typical. Even at very low levels, care must be taken to avoid combinations of tertiary amines with simple phenolic antioxidants (e.g., BHT) or with hydroxybenzophenone UV light absorbers. With catalysis by trace hydrogen chloride from degrading PVC, amine/phenol combinations, even at low concentrations, can generate unwanted coloration in a broad spectrum of hues. These effects can be avoided by use of benzotriazole UV light absorbers, and employment of phenolic antioxidants whose structure does not permit oxidation to quinones or coupled quinoid products. In an analogous manner, tertiary amines can also influence decomposition of chemical foaming agents, particularly azodicarbonamide.

Titanates and Zirconates These additives, typically used as coupling agents, have been proposed as (presumably nonionic) antistats for filled PVC and other polymers.[18] It is possible that they function also by creation of polar, hydrogen-bonded surface layers after migration to the surface and partial hydrolysis. In filled compounds generally, it is useful to treat the filler (or use pretreated filler) before addition of antistats. This is particularly the case with polyol esters. The underlying principle is that the compound should not contain ingredients that could compete successfully for antistats.

Stannous Stearate Another lubricant that imparts antistatic properties is stannous stearate. Most polyvalent metal carboxylates form associated structures in semipolar media (e.g., PVC compounds) that involve carboxylate bridges.[19] Metals, such as tin, that can expand their octet are ideal for generating bridged, hydrogen-bonded networks through migration to the surface and absorption of atmospheric moisture. In contact with moist air, there is probably also oxidation to Sn(IV). Whether or not this occurs, surface layers of "stannous" stearate resist dehydration and removal by abrasion. In addition, stannous stearate has lubricant and secondary stabilizer properties. The expense of this additive has generally limited its use to demanding applications, such as mining belts.

12.6.3.2 Ionic Antistats Ionic antistats are described as "cationic" or "anionic" as if the corresponding part of the additive were wholly responsible for the effect, and the counterion included only to provide electrical neutrality. Such a view is naive. In nonionizing media (e.g., PVC compounds), ionic species are present as solvated tight ion pairs (or groups). Both ions are important in surface static charge decay (as well as in nonaqueous surfactant technology). Changing the anion of a "cationic" antistat, or the cation of an "anionic" one, is certain to affect performance.

Cationic Antistats Quaternary ammonium salts are considered cationic antistats: $R_4N^+X^-$. Usually the four R groups contain one long-chain alkyl group, the remainder, methyl or ethyl. The anion is typically methyl- or ethylsulfate $(R'{-}O{-}SO_3)^-$. On reaching the surface and moist air, the additive is in equilibrium with hydrolysis products: tertiary amine, alcohol, sulfuric acid, and recombinations. Amine oxide formation is also possible. The surface layer is, therefore, a hygroscopic layer of high ionic strength. These agents are stronger antistats than nonionics, permitting use at lower levels. This stems from their not having to wait for ionic detritus from the atmosphere. It is a fortunate consequence, as few PVC compounds can tolerate more than traces of additives as acidic as amine alkylsulfates. This class of antistats should be used guardedly with compounds containing barium/cadmium or barium/zinc stabilizers because of the probability of forming unreactive barium sulfate.

Similar, but more efficient, are ethoxylated quaternary ammonium salts: $R_2N^+(CH_2CH_2OH)_2X^-$. The popular anions are alkylsulfates and *p*-toluenesulfonate. As with ethoxylated amines, there is an increased tendency to form a hydrogen-bonded surface network relative to simple quaternary salts. This class of cationics tends to provide the greatest resistance of all internal antistats to build of surface resistivity with decreasing relative humidity. This is simply from the difficulty in dehydrating aqueous sulfuric or toluenesulfonic acids without resort to extreme conditions. The effect of additives in this category on heat stability must be investigated carefully before proceeding with their use in PVC.

A subclass employs a substituted amide group in place of one of the two hydroxyethyl groups on nitrogen. Amides are also excellent participants in hydrogen-bonded networks. Known as amidoamines, these products use nitrate and dibasic phosphate anions. This group is somewhat less prejudicial to PVC heat stability. Nonetheless, care must be taken when used in concert with stabilizers based on barium or lead. Dibasic lead phosphate (as opposed to dibasic lead phosphite) is not a very good stabilizer. Furthermore, insoluble salt products of such reactions may influence plateout and die buildup characteristics negatively. It is always disconcerting to have desirable additives, placed in a formulation to overcome certain deficiencies, conspire among themselves to generate new ones.

Anionic Antistats Anionic antistats for PVC include sodium salts of alkyl sulfonates and phosphates. These additives are, in addition, external lubricants. In some cases, their inclusion may boost stabilizer activity (as with lubricants in general). Generally, their use poses less of a hazard to heat stability than amine salts of strong acids. At more than trace levels, adjustments to the overall stabilizer and lubricant package are usually needed. Usage with barium or lead must also be checked, as noted above, for unexpected effects.

12.6.4 External Antistats

There are two advantages gained in using external antistats: The additive may be placed directly on the surface, rather than arriving there by hoped-for migration. Secondly, interference with other additives (e.g., stabilizers) during mixing and processing is avoided. The materials used include all of the ionic surfactants discussed above. Instead of polyol esters, nonionics comprise the actual polyols, notably polyalkylene glycols. These agents are applied from dilute aqueous or alcoholic solutions by a range of coating procedures. Principal PVC articles so treated include rigid profiles and bottles.

To be successful, the external antistat must have the compatibility associated with an external lubricant. That is, it must adhere strongly enough to a clean PVC surface to develop resistance to being removed by the frictional contact that would otherwise generate static charge. At the same time, it should not be so compatible as to migrate into the compound and disappear from the surface. In actual practice, this balance is rarely met. More often, the external antistat will both dissolve into the compound and be remainder wiped off within days or weeks.

A monomeric coating of a quaternary ammonium salt has been reported to lower the surface resistivity of rigid PVC film by three orders of magnitude with only minor effects on heat sealability.[20] Nonetheless, both internal and external antistats may affect other surface properties in an undesirable manner, for example, interfere with printing or label adhesion, or corrode adjacent metal surfaces. Generally external antistats are more troublesome in these regards. The technology to compensate for these effects (e.g., by formulating inks or adhesives to penetrate such layers) is available, although not always practiced.

12.6.5 Effect of Other Ingredients

PVC Resin All other factors being equal, the PVC polymer with the highest content of residual ionic species from the manufacturing process will yield the lowest surface resistivity. A further consideration is polymer viscosity. The lower the viscosity, that is, the lower the molecular weight, the greater the mobility of small-molecule additives. The choice of resin is, however, governed by the application. The technologist should select the grade of PVC most appropriate to the product and process, with use of additives to provide the needed surface resistivity.

Plasticizers Polar plasticizers such as esters decrease surface resistivity of nonblack compounds; hydrocarbon secondary plasticizers provide increased levels. Unplasticized PVC without a surface coating of paraffin wax has a surface resistivity of about 10^{13} ohm.[21] Addition of 40 phr of ester plasticizer decreases this to 10^{10}–10^{11} ohm.[22] Phosphate plasticizers can lower surface resistivity by several orders of magnitude.[23] In addition, the mobility (lowering of glass transition temperature) of the plasticizer is a factor. Low-temperature plasticizers are found to have an increased effect in lowering surface resistivity.[22] When substituting, for example, an adipate or oleate for a phthalate to lower surface resistivity (in cases where the application permits), it must be considered that the former are more available microbial nutrients.

Stabilizers With ionic antistats, it is necessary to avoid reactions with heavy metals that form insoluble salts, such as the use of sulfates with barium or of phosphates with lead. Oxidizing anions such as nitrates should not be used with organophosphites or divalent sulfur secondary antioxidants (e.g., DLTDP). As with choice of resin and plasticizer, product and process considerations determine stabilizer selection, and antistatic behavior is usually secondary.

Fillers The development of a charged layer at the filler particle surface with shear during mixing is important in achieving rapid incorporation and good dispersion. Therefore, antistatic agents should be added after filler incorporation. Charge-dissipating fillers, such as graphite or boron nitride, are, as a result, more difficult to incorporate without forming agglomerates, and are often used as concentrates. The problem is avoided with metal oxide and hydroxide fillers by use of coupling agents.

High-surface-area fillers, such as fine-particle grades of silica or clay, should also be surface-treated when used with antistats to avoid surface adsorption of the latter. Conductive carbon black and magnetic iron oxide typically provide adequate charge dissipation. Addition of antistatic agents should be avoided with these so as not to interfere with their function.

12.6.6 Applications

Injection Molding In a typical pipe fitting compound, the use of polyol antistats led to high surface resistivity, 10^{15} ohm, even at 10 phr.[24] Use of amine or amide antistats at 5 phr produced surface resistivity of 10^9–10^{14} ohm, depending on the actual product used. The most powerful quaternary ammonium salts, at 3.5 phr, gave values of 10^9–10^{11} ohm. Such levels are, however, prejudicial to physical properties and heat stability. In many cases, the only effect desired is that static not interfere with air conveying of pellets, for which the following has been suggested:[25]

PELLETIZED COMPOUND FOR INJECTION MOLDING

PVC	100
Impact modifier	3
Organotin mercaptide	1.5
Paraffin wax	0.5
Calcium stearate	0.8
Polyol antistat	0.1

Packaging Film Typical examples of rigid food packaging films often use combinations of GMO and ESO:[26]

RIGID PACKAGING FILM

PVC copolymer	100
Impact modifier	8–12
Ca/Zn stabilizer	2–3
GMO	0.5
ESO	5

In such compounds, the surface will have a layer of ESO–GMO, adsorbed water and ionic components from the atmosphere, and possibly calcium chloride from stabilizer action. Food packaging films are restricted to FDA-sanctioned ingredients, tending to limit usage to polyol esters, GMO where high clarity is needed, and otherwise GMS. If radiation sterilization is anticipated, an FDA-sanctioned antioxidant is added, mainly to protect the GMO–ESO combination.

Semirigid and flexible packaging films are similar in antistatic design:[26]

SEMIRIGID AND FLEXIBLE PACKAGING FILMS

PVC	100
DOA or similar	7–20
Zinc phosphite stabilizer	2–3
Stearic acid	0–0.5

ESO	7–10
GMO or GMS	0.5–1
EBS	0–0.3

The use of low-temperature plasticizers in such products enhances antistatic behavior, as does the high level of ESO and addition of EBS. Surface resistivity is lower than with use of more polar plasticizers. The choice of organophosphite for such compounds should reflect plasticizer selection, that is, be of comparable polarity. In FDA-sanctioned compounds, phosphite choice is unfortunately narrow.

With packaging films, the objective is to provide products that do not generate sufficient static charge to interfere with packaging. Suitable levels of surface resistivity typically also provide protection from water fogging.

Footware The following compound has been suggested for static-resistant shoe soles:[27]

STATIC-RESISTANT SHOE SOLES

PVC	100
NBR elastomer	30
DINP	80
ESO	10
Filler, carbon black	6
Stearic acid	1
Calcium stearate	0.2
Stabilizer	2
Ethoxylated amine	6

The addition of ethoxylated amine antistat lowered surface resistivity two orders of magnitude, to the range of 10^6–10^7 ohm, a reasonable level to provide protection from spark discharge from friction. In areas where combustible dust is a hazard, shoe soles are instead semiconducting.

Floor Tile Highly filled vinyl composition tile is an area where quaternary ammonium salts can be used to provide charge dissipation, such as in the following example:

CHARGE-DISSIPATING FLOOR TILE

PVC	100
Phthalate plasticizer	28
Stabilizer	5
Calcium carbonate(s)	625

Hydrocarbon resin	9
Pigment(s)	12
Quaternary ammonium salt	12

Compounds such as the above are installed using semiconducting adhesives and protected from water absorption by coating with polishes containing antistatic agents. The combination of charge dissipating flooring with suitably formulated shoe soles and equipment stands is effective in preventing spark discharge at relatively normal percent RH.

Carpet Underlay The area of conductive carpet and work mat underlay is one of the few where semiconducting carbon is used with antistatic agents, as in the following:

CONDUCTIVE CARPET UNDERLAY

PVC	100
NBR	30
Phthalate plasticizer	65
Conductive carbon black	28
ESO	4
Stabilizer	1.5
Stearic acid	0.75
GMO–GMS blend	4.5

A surface resistivity of 10^3 ohm is reported. The use of high stearic acid levels, as in the shoe sole example, is common with NBR blends. Similar plastisols containing antimony oxide for flame resistance are used to coat fabric reinforcements for mining belt covers.

Wall Coverings Plastisol wall covering compounds tend to use 3–5 parts of polyol esters to limit dust pickup:

PLASTISOL WALL COVERING

PVC	100
DIDP	50–60
Calcium carbonate	25–40
Pigment(s)	5–15
Stabilizer	2–3
ESO	3–5
Biocide concentrate	0.2–0.5
Polyol ester	3–5

Calendered wall coverings use similar levels of polyol antistats. Higher levels will tend to defeat the effects of biocidal additives.

Clear Plasticized Compounds Typical instrument or computer covers are protected from undue dust pickup and static cling with polyol antistats:

CLEAR DUST COVER

PVC	100
Phthalate plasticizer	50–60
ESO	4–5
GMO	3–5
EBS	0.1–0.2
Stabilizer	2–3

The internal components of the instrument are protected from damage by grounded conductive shields. Nevertheless, nearby static discharge must be avoided. Strip curtain doors are similar except for somewhat lower plasticizer levels and inclusion of biocide concentrates.

12.6.7 Test Methods

The magnitude of surface charge and decay with time can be measured with high accuracy using a Faraday cage per ASTM D 2679. The apparatus consists of a hollow cylindrical inner electrode separated by insulating spacers from a concentric outer electrode, which is grounded. A sheet of sample is frictionally charged and placed within the apparatus, inducing a potential across the electrodes, which is read with a sensitive electrometer, and decay plotted versus time. Per Federal Standard 101B, Method 4046, the sample is charged to 5000 V and the time measured for a drop to 500 V, the "10 percent cutoff time." The equipment is sold as the Static Decay Meter (Electro-Tech Systems). For products used in hospital operating rooms or hazardous environments, the National Fire Protection Association (NFPA Code 56A) requires the 10 percent cutoff time to be reached within 0.5 s at 50 percent RH.

Surface resistivity is determined per ASTM D 257, using a Wheatstone bridge or an electrometer. Hand-held meters are useful only to 10^{12} ohm, above which they are affected by vibration and air currents. At 50 percent RH, 10^9 ohm corresponds to a 10 percent cutoff time of about 0.01 s; 10^{10} ohm, about 0.1 s; 10^{11} ohm, about 0.2–0.5 s; 10^{12} ohm, about 1 s. Above this level, static dissipation is slow.

A number of ad hoc methods have been used to estimate charge level and rate of dissipation. These should be disregarded in favor of ASTM Standards or their international equivalents.

12.6.8 Antifogging Agents

The failure of atmospheric water to wet the surface of a film and instead to condense as small droplets is referred to as fogging, since it obscures the clarity of the film. The development of a hydrophilic surface that is readily moisture-wettable is completely analogous to providing antistatic properties. Film for packaging applications generally uses glycerol or sorbitan esters; PVC greenhouse glazing tends toward more UV-light resistant polyol esters, such as those based on pentaerythritol. Although various ad hoc tests have been used to determine whether condensate will fog a film surface, the best procedure is to measure the contact angle with water, noting the speed with which the contact angle drops to near zero as the drop wets and spreads. Although contact angle should relate to surface resistivity, such correlation does not seem to have been reported.

12.7 ADHESION PROMOTERS

Adhesion promoters (basically antilubricants) are used mainly in PVC plastisols and coatings to improve bonding to fabrics, metals, or glass. In these applications, many of the additives discussed above, such as external lubricants and slip agents, must be omitted or used at trace levels. Other cautions will be mentioned with regard to specific adhesion promoters.

Urethanes Urethane adhesion promoters are used widely to bond PVC to polyester, nylon, and other fabrics, including sized glass fiber. In multicoat operations, the additive is used only in the first coat. With, polyester fabric, the isocyanate component in urethane formation can be used alone. Solvent or plasticizer solutions of oligomerized toluene diisocyanate (TDI) are available under the trade names Vulcabond® (Akzo Nobel), Vanchem® HM-50 (Vanderbilt), Thanecure® T9 (TSE Industries), and Desmodur® (Bayer). For improved resistance of the bond to heat and moisture, products based on bisphenyl diisocyanate (MDI) are also used. These include Vanchem® HM-4346 and Rubinate® 9480 (Huntsman). These are typically used at 3–7 phr levels in plastisols for coating polyester fabric. The second or subsequent coats should contain titanium dioxide and UV light stabilizer for outdoor service. With translucent products, an aliphatic isocyanate such as Desmodur® N-100 or TMI® META (Cytec) should be used.

With fabric substrates other than polyester, such as nylon, both urethane components are added: the isocyanate as above, plus 3–8 phr of a solution of a reactive polyester, such as Bonding Agent TN (Bayer), Grip-Gard® (Akzo Nobel), or Cythane® 3174 (Cytec). In such cases, additives that are strong urethane catalysts, such as organotin stabilizers or foam kickers, will drastically reduce pot life. In all cases, isocyanate-reactive additives should be avoided. This class includes stearic and other acids, stearyl alcohol, β-diketone costabilizers, and polyols; that is, compounds containing reactive hydrogen. It is also desirable to use simple lubricants such as paraffin and calcium stearate. Ester and amide lubricants may consume isocyanates. As a result, it is usually best to use a first coat designed for adhesion, then overcoat with a more generally suitable compound.

The typical mixing procedure is to add the polyester component first, and the isocyanate just before usage. Glass fiber may be similarly coated if previously sized with an aminosilane.

Aminoamides Polyaminoamides are used to improve bonding of PVC plastisols to metal surfaces. Used at 3–5 phr, generally dissolved in solvent or plasticizer, such products are available under the trade names Euretek® (Schering) and Versamid® (Henkel = Cognis). The bond formed is to the surface metal oxide layer. Combinations with urethane adhesion promoters should not be used, since the aminoamides are strong urethane catalysts. A topcoat (without adhesion promoter) is usually desirable; it should be formulated to resist amine stain. Phenolic antioxidants used with aminoamides (or other amine additives) should have all *ortho* and *para* positions blocked to prevent color development on aging. Similarly, aliphatic phosphites are the best choice.

Coupling Agents Coupling agents are the adhesion promoters of choice for use with glass fiber. They will also react in some cases with metal oxide surfaces. The coupling agent should contain a group that displaces labile chloride from PVC, actually bonding the additive to the polymer. The best resistance to heat aging is obtained with mercaptide functional groups. Mercaptosilane coupling agents are available from GE (A-189 and A-1891), Dow Corning (Z-6062), PCR (Prosil® 196), and Degussa (CM8500). Mercaptozirconates are available from Mannchem (MOD® S). Of the above, A-189, Prosil 196, CM8500, and Z-6062 are trimethoxy mercaptosilanes, which will react rapidly with clean glass or metal oxide surfaces rapidly. A-1891 is a triethoxy mercaptosilane, which reacts more slowly but provides longer pot life and more stable viscosity, as is also true of the mercaptozirconate MOD S. The last is a solution (23 percent) in isopropyl alcohol, the others are undiluted.

Despite the advantage of good heat stability, the odor of mercaptide coupling agents, although not present in the final product, has nevertheless militated against their use in flexible PVC. In practice, aminofunctional coupling agents are mostly used. They are divided into monoamino additives, which provide the best pot life, and polyamino, which create the highest level of adhesion. Monoaminosilanes are available from GE (A-1100 and A-1110), Dow Corning (Z-6020), Degussa (CAO750), and PCR (Prosil® 221). Polyaminosilanes are available from GE (A-1120 and A-1130), Dow Corning (Z-6050), Degussa (CT2910), and PCR (Prosil® 3128). Polyaminozirconates are available from Kenrich (LZ® 44) and Mannchem (MOD® A); polyaminotitanates from Kenrich (LICA® 44). MOD A is a solution (24.5 percent) in isopropyl alcohol, the others are undiluted. Silanes are typically used at 0.25–1.0 phr; with titanates and zirconates, the suppliers should be consulted.

The traces of moisture found in plastisols and coatings exposed to the atmosphere are sufficient to hydrolyze the trimethoxysilane group and provide for bonding to —OH on the surface of glass or metal oxide coating. With modest heat input, the same is true of the less reactive triethoxysilane group. Desiccants such as calcium oxide may, therefore, interfere with coupling agent adhesion promoters. On the other hand, excess water will condense the coupling agent and form intractable lumps. Hydrous fillers and zeolite-containing stabilizers should be avoided in this application or surface-treated prior to incorporation. The coupling agent is often dissolved in the plasticizer to avoid high local concentration.

With filled compounds, it is necessary to avoid consumption of the adhesion promoter through coupling instead to the filler surface. Thus, calcium carbonate is the preferred filler with silane adhesion promoters. Calcined clay or ATH may be used if previously silane-treated. Compounds containing reactive silanes should be processed promptly. The use of titanates or zirconates as adhesion promoters should be carried out in close cooperation with the additive supplier.

Reactive Monomers Plastisol adhesion to steel can be improved by using a combination of reactive monomer and a low level of organic peroxide to provide crosslinking. As a general rule, crosslinking improves polymer adhesion to polar surfaces. Note, for example, the tenacious adhesion of crosslinked polyethylene (XLPE) to metal conductors, as compared with thermoplastic LDPE. Typically, 5–15 phr of ester plasticizer are replaced with trimethylolpropane trimethacrylate (TMPTMA) or special purpose reactive monomer. Proprietary products, such as SB-600™, are available from Sartomer Corp. The organic peroxide t-butyl perbenzoate is used at about 0.5–1 phr. For lower odor, about two-thirds as much 2,5-dimethyl-2,5-diperbenzoate (Varox® 118, R.T. Vanderbilt) may be used instead. (Note that combinations of organic peroxides often show interactive decomposition, and should be well investigated before use.)

Peroxide-initiated reaction of the multifunctional monomer traps polymer chains, building tensile strength and low extension modulus. This leads to higher adhesion to substrates that are wet by the composition; that is, the energy needed for removal by peel or shear is markedly increased. The process succeeds because the reaction of the monomer is more rapid than peroxide-initiated degradation of PVC. The perbenzoate-reactive monomer system also predominates over side reactions that normally consume peroxide, such as with organic acids, phosphites, or antioxidants. In foamed products, however, organic peroxides may alter blowing agent decomposition; such effects must be investigated prior to actual use. As a safety precaution, monomer and peroxide should be added separately to the compound, never premixed.

12.8 COMMERCIAL PRODUCTS

The following list of products is not intended to be exhaustive, but rather representative of usage in PVC in the United States. Nomenclature as well as usage is dynamic. Therefore, it is advisable to contact suppliers as to whether those listed have been superseded by others. Where more than one grade is offered, the intended applications for diverse grades should be determined. Lastly, it must be remembered that grades listed as equivalents are so for most, but not for all, applications. Paraffin waxes, both refined from petroleum and synthetic Fischer–Tropsch, are listed in Table 12.1. The first three products of Table 12.1 derive from the Fischer–Tropsch process, the remainder from petroleum. It should be noted that many distributors also carry these products. MP is, of course, published softening, not melting, point. For purposes of compound cost calculation, the specific gravity of paraffin wax may be taken as 0.92. PE waxes are listed in Table 12.2. Oxidized

TABLE 12.1 Hydrocarbon Waxes

Supplier	Trade Name	Type
Hoechst	Hostalub XL165	MP 165 °F (74 °C)
	Hostalub XL200	MP 200 °F (93 °C)
	Hostalub H4	Oxidized
C.P. Hall	IWL-1262	MP 165 °F (74 °C)
Rohm & Haas	Advawax 165	MP 165 °F (74 °C)
Penreco	Parol 100	Mineral oil
Petrolite	C-1035	MP 200 °F (93 °C)
Chemtura	Sunolite 160	MP 160 °F (71 °C)
	Kaydol	Mineral oil
Ferro	Petrac 165	MP 165 °F (74 °C)

grades and copolymers should be assumed to have a specific gravity of 0.93, otherwise 0.92. Certain copolymers may run as high as 0.94 and some others as low as 0.91, but, at the low level of use, this will not affect cost calculations.

Carboxylic acids of various types used as lubricants in PVC are listed in Table 12.3. Many of these are also available through distributors. Relevant specific gravities are as follows: stearic acid, 0.94; oleic acid, 0.89; tall oil fatty acids, 0.88; lauric acid, 0.87; 12-hydroxystearic acid, 0.91; palmitic acid, 0.87; montanic acid, 0.99.

Commercially available amide lubricants are listed in Table 12.4. For cost calculations, the specific gravity of EBS is 0.97; the others may be taken as 0.88.

TABLE 12.2 Polyethylene Waxes

Supplier	Trade Name	Type
Allied Signal	AC 6A	MP 222 °F (106 °C)
	AC 617A	MP 215 °F (102 °C)
	AC 629A	Oxidized, MP 219 °F (104 °C)
	AC 392	Oxidized, MP 280 °F (138 °C)
	AC 430	EVA copolymer
	AC 540	Acid copolymer
Hoechst	PE 130	MP 260 °F (127 °C)
	PE 520	MP 253 °F (123 °C)
	PE 190	MP 284 °F (140 °C)
	PED 521	Oxidized, MP 230 °F (110 °C)
Eastman	C-10P	MP 219 °F (104 °C)
	N-14P	MP 223 °F (106 °C)
	E-14P	Oxidized, MP 219 °F (104 °C)
Petrolite	Polywax 655	MP 215 °F (102 °C)
	Polywax 850	MP 228 °F (109 °C)
Ferro	Petrac 215	MP 215 °F (102 °C)

TABLE 12.3 Carboxylic Acids

Supplier	Trade Name	Type
Akzo Nobel	Neo-Fat 12	Lauric acid
	Neo-Fat 18	Stearic acid
Arizona Chemical	Actinol FA-2	Tall oil fatty acids
Chemtura	Hystrene 9512	Lauric acid
	Hystrene 9718	Stearic acid
	Hystrene 5016	Palmitic acid
	Industrene 106	Oleic acid
	Industrene 224	Tall oil fatty acids
Ferro	Petrac 270	Stearic acid
Hoechst	Hoechstwax S	Montanic
Henkel (Cognis)	Emersol 420	Stearic acid
	Emersol 652	Lauric acid
	Emersol 213	Oleic acid
Lonza	Glycon S-65	Stearic acid
SCM Chemicals	Sylfat 95	Tall oil fatty acids
Sherex	Hydrofol 1865	Stearic acid
Unichema	Priolein 6910	Oleic acid
	Prifac 2922	Lauric acid
	Prifac 9428	Stearic acid
Union Camp	Century 1005	Oleic acid
	Century 1250	Stearic acid
	Cenwax A	Hydroxystearic acid

TABLE 12.4 Amide Lubricants

Supplier	Trade Name	Type
Akzo Nobel	Armoslip 18	Stearamide
	Armoslip EXP	Erucamide
	Armoslip CPM	Oleamide
Akcros	Interstab G-8257	EBS
Chemtura	Kenamide S	Stearamide
	Kenamide O	Oleamide
	Kenamide W-40	EBS
	Kenamide W-20	EBO
Hoechst	Hostalub FA-1	EBS
Lonza	Acrawax C	EBS
Rohm & Haas	Advawax 280	EBS
	Advawax 240	EBO
Sherex	Adogen 58	Erucamide

TABLE 12.5 Ester Lubricants

Supplier	Trade Name	Type
Akcros	Interstab G-140	GMS
Ferro	Petrac GMS	GMS
Hoechst	Hostalub FE-71	GMS
	Hostalub FE-76	GMO
	Wax E, 4, OP	Montanate esters
Henkel (Cognis)	Loxiol G10	GMO
	Loxiol G11	Glyceryl hydroxystearate
	Loxiol G12	GMS
	Loxiol G16	Gyceryl dioleate
	Loxiol G33	Stearyl stearate
	Loxiol G60	Distearyl phthalate
	Loxiol G70	PE adipate-stearate
	Loxiol G71	PE adipate-oleate
	HOB 7119	PE tetrastearate
	HOB 7121	PE mono/distearate
Lonza	Aldo MS	GMS
	Aldo MO	GMO
	Glycolube 8	Glyceryl caprylate
	Glycolube P	PE tetrastearate
Rohm & Haas	Advawax 140	GMS
Scher Chemical	Schercemol GMS	GMS
	Schercemol 1818	Stearyl stearate
Union Camp	Uniflex BYS	Butyl stearate
Unichema	Estol 1407	GMO
	Estol 1451	Butyl stearate
	Estol 1458	Iso-octyl stearate
	Estol 1462	GMS

TABLE 12.6 Metal Carboxylate Lubricants

Supplier	Product
Addenda	Dibasic lead stearate
	Normal lead stearate
Chemtura	Calcium stearate
	Zinc stearate
	Barium stearate
Ferro	Calcium stearate
	Zinc stearate
	Barium stearate
Halstab	Dibasic lead stearate
	Normal lead stearate
	Barium stearate
	Zinc stearate
Hoechst	Calcium montanate
Mallinckrodt	Calcium stearate
	Zinc stearate

TABLE 12.7 Polyol Ester Antistats

Supplier	Trade Name	Type
Chemax	Chemstat	Glyceryl esters
Chemtura	Markstat	Proprietary
Hoechst	Hostastat	Glyceryl esters
ICI	Atmer	Glyceryl esters
	Span	Sorbitan esters
	Tween	Sorbitan derivatives
Lonza	Aldo	Glyceryl esters
	Glycomul	Sorbitan esters
PVO Intl	Drewplast	Glyceryl esters

TABLE 12.8 Amine Antistats

Supplier	Trade Name	Type
Alframine	Electrosol	Fatty amine
Akzo Nobel	Armostat 310	Stearylamine
	Armostat 410	Cocoamine
Chemtura	Markstat	Proprietary
Hexcel	273-C	Cocoamine
	273-E	Stearylamine
Hoechst	Hostastat FA 14	Cocoamine
	Hostastat FA 18	Stearylamine
ICI	Atmer 163	Fatty amine

TABLE 12.9 Ionic Antistats

Supplier	Trade Name	Type
Chemax	Chemstat	Cationic, amine salts
Chemtura	Markstat AL	Cationic, amine salts
Cytec	Cyastat LS	Cationic, amidoamine
	Cyastat SN, SP	Cationic, hydroxyamine
GAF	Gafac	Anionic, phosphates
Hexcel	106-G	Cationic, hydroxylamine
Hoechst	Hostastat HS	Anionic, sulfonate
Jordan	Larostat	Cationic, amine salts
Kenrich	KenReact	Titanates, zirconates

Ester lubricants are listed in Table 12.5 and metal carboxylate lubricants in Table 12.6.

Commercially available polyol ester antistats are listed in Table 12.7; amine antistats in Table 12.8 and ionic antistats in Table 12.9.

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CHAPTER 13

Plastisol Technology

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13.1 INTRODUCTION

Plastisols are dispersions of special purpose vinyl resins in plasticizer. It is presumed that processing into finished articles will leave all but traces of the plasticizer in the compound; that is, that volatilization will be small (Section 1.5). If the flow of the compound is assisted by adding solvent, a "plasticizer" that will volatilize during processing, it is referred to instead as an organosol. The dividing line between the terms is generally taken that an organosol has more than a few percent (e.g., >5 percent) solvent. Actually, the term "solvent" is a misnomer in this connection. It is not expected that the "solvent" will dissolve the resin; this would increase viscosity and, with relatively high-molecular-weight emulsion resins used with plastisols, impede processing. The "solvents" used in plastisols and organosols have very limited swelling action on the resin, and instead reduce viscosity of the dispersion. They are, therefore, properly volatile diluents in their action. As a result, the term "modified plastisol" is sometimes used to describe such compositions. Note that with lower-molecular-weight solution resins, solvents are used in the classical sense of vehicles to dissolve resin. Resin selection for use with true solutions is presented in Section 3.2 and that for plastisol use in Section 2.5.

Dispersion resins for plastisols are of very fine particle size (1–2 μm) as compared with suspension resins intended for general purpose compounding, leading to rapid dispersion in plasticizer. They are often used with a minor fraction of larger-particle

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PVC, referred to as a blending resin. The effect of broadening particle distribution of the resin blend is to decrease the fraction of plasticizer consumed in filling resin voids, increasing the fraction available for dispersion. The result is lower and more stable viscosity, with regard both to shelf aging and to the effect of shear rates encountered in mixing and processing. The use of larger particles also increases the tendency to settle, and may reduce mechanical properties, clarity, gloss, and speed of gelation. Vinyl acetate copolymer resins have also been used; such plastisols have lower gelation and fusion temperatures than analogs with homopolymers, but may have increased viscosity because of higher solubility in the plasticizer.

The two most important considerations in formulating plastisols are resin and plasticizer selection. General purpose (GP) plasticizers, such as DOP, tend to yield reasonable plastisol viscosity and handling throughout a range of concentration. Aliphatic diesters, such as adipates and cyclohexane carboxylates, provide lower viscosity than GP grades, as do linear phthalates. Plasticizers of low volatility, such as DIDP, typically yield higher viscosity than GP grades. Fast-solvating plasticizers, such as DHP and BBP, yield plastisols that develop higher viscosity because of swelling of resin particles. Secondary hydrocarbon plasticizers provide low viscosity, but are limited to low levels (except in organosols) because of marginal vinyl compatibility. As with all formulating, ultimately desired mechanical and aging properties needed by the application determine plasticizer type and level. The effects of formulating so as to provide required properties are accommodated by the processor through selection of resin and other additives, and by choice of processing conditions.

As with vinyl generally, most filled compounds are based on calcium carbonate. With typical 1–2 μm grades, loadings of up to or slightly higher than the plasticizer content, have the effect of yielding increases in plastisol viscosity that are tolerable in most processing, typically decreasing with shear rate. This is often not the case if submicron grades of calcium carbonate (or other filler) are used. As a general rule, fillers with higher oil absorption, finer particle size, and more irregular shape will yield higher viscosity. Other fillers that have been used include barytes, for sound absorption because of high density; calcined clay, for electrical properties; and hydrous fillers for flame resistance and smoke suppression (Sections 16.3 and 16.4). Grades of titanium dioxide used for pigment and UV light absorption increase plastisol viscosity in the levels most often encountered (2–8 parts per hundred of resin (phr)), but typically not to an extent that would prejudice processability. Fine-particle carbon black, on the other hand, may be expected to yield major increases in viscosity. Since in either case a high level of dispersion is needed, the use of plasticizer paste dispersions is well worth considering. Flame retardant (FR) additives require intimate additive–resin contact for effective operation; it is, therefore, not surprising that FR additives such as antimony oxide and hydrous fillers (ATH and BMC) increase both viscosity and build of viscosity on standing.

Stabilization systems for plastisols are discussed under specific applications in Section 4.4. Powder mixed metal stabilizers or powder boosters are often added with filler, and may be, as a result, preferred with compounds of substantial filler loading. Liquid mixed metal or organotin stabilizers are typically added with (or to) the plasticizer. As discussed in Chapter 4, there is no longer any compelling reason to consider stabilizers based on lead or cadmium in vinyl; this applies as well to plastisol formulation. Since heat stabilizers for plasticized vinyl commonly have pronounced surface-active properties, a change in stabilizer may have a marked effect on plastisol viscosity. This is also true of lubricants and related additives (Chapter 12).

Inclusion of polymers of relatively high molecular weight or elastomeric character, such as NBR, will usually drastically increase plastisol viscosity. These may be more conveniently dealt with as latex blends (Chapter 3). Formulators generally should consider latex, solution and plastisol compounds as a broad single field to draw on for various applications.

13.2 RHEOLOGY CONTROL ADDITIVES

In plastisol and organosol formulation, as is also the case with vinyl latex and solutions, the technologist is concerned with processing a multiphase system prior to gelation and fusion, but that is where processing usually ends. This is distinct from formulation of "dry" compounds, where processing usually continues after the composition has fused; that is, that shaping into articles is accomplished after, rather than prior to, fusion. This both limits and provides opportunity for the plastisol formulator.

A variety of additives are used to lower plastisol viscosity; these are referred to as viscosity depressants. They are typically surfactants that reduce the surface tension of the plasticizer, perhaps selectively at the interface with resin and with filler. The simplest are alcohols such as 2-ethylhexanol (2-EHA) and isodecyl alcohol (IDA). They are commonly used with the corresponding ester plasticizers: 2-EHA with, for example, DOP or DOA; IDA with DIDP. At a 1–3 phr level, viscosity and, particularly, viscosity build are reduced. Both are volatile and lost during fusion and, therefore, have little negative effect on fused compound properties. On the other hand, they have distinctive odors that may be unattractive during processing. In some instances, the traces remaining after fusion may be found unattractive.

Additives used as compatibilizers in liquid stabilizers are also used as viscosity depressants, for example, ethylene glycol monobutyl ether (Butyl Cellosolve®) or diethylene glycol monobutyl ether (Butyl Carbitol®, both Dow Chemical). At a 1–3 phr level, they are more effective in reducing viscosity and viscosity build than aliphatic alcohols. (It must be kept in mind that such generalizations may be influenced by choice of plasticizer and resin, and, therefore, have exceptions.) Glycol ether surfactants may or may not be completely fugitive on fusion. If present after processing, there will be discernible odor.

Permanent, nonvolatile surfactants also find use, typically at 1–2 phr. These include ethoxylated nonylphenol derivaties such as Tergitol® NP-10 (Dow) or Igepal® CO-520 (Rhodia) (CAS 127087-87-0). These may add to heat stability of compounds stabilized with overbased calcium or barium nonylphenates (Section 4.4.2). Nonylphenate-based surfactants (as well as stabilizers) are sensitive to nitrogen oxide (acid gas) discoloration, a factor that must be balanced against their effectiveness in viscosity reduction. For the best color hold, it may be preferable to use aliphatic nonionic surfactants based on polyglycols, such as Pegosperse® 400 MO (PE glycol monooleate; CAS 9004-96-0) and 400 LM (PE glycol monolaurate; CAS 9004-91-3) (both Lonza), or polyol esters such as Polysorbate® 80 (CAS 9005-65-6) (BASF). All of these are nonfugitive during processing, but are useful as filler treatments, air release agents and foam structure improvers in expanded plastisols. Ionic surfactants have occasionally been used, most frequently those based on sodium salts of tauric acid, of the general formula $RCONR'—CH_2CH_2—SO_3H$, available under the trade names Igepon® (Rhodia) and Hostapon® (Clariant). These are particularly useful in preparing plastisols where filler dispersion is a problem. They may also help the performance of surface antistatic agents, as is also likely with polyol-based surfactants. Compounds containing persistent viscosity depressants should be checked for long-term heat stability and possibility of exudation.

Plastisol foam stabilizers (Section 14.5) may also function as viscosity depressants. With foamed plastisols, these factors must be considered together. Conversely, the viscosity depressants listed above typically also function as air release agents. Silicone additives can assist in all three areas, but must be used with caution if operations, even on other lines, involve applications requiring adhesion, printing, or decorating. It makes no sense to have unreasoning prejudice against such additives, but rather to be certain that they are used properly.

In some applications, plastisols must have their viscosity increased rather than depressed. These include fabric coatings where strike-through is not desired and sealants that must resist sag during setting. In many such cases, high viscosity at low shear rate, but low viscosity at higher shear rates, is needed. With plastisols highly filled with calcium carbonate, this effect can usually be achieved with calcium carbonate grade selection. The customary 1–2 μm grades provide considerable viscosity increase when used, for example, at the same level as ester plasticizer. Coarse grades in the 8–10 μm range have only a minor thickening effect, but precipitated submicron grades with high oil absorption values (>20 g/100 g) provide major increases in viscosity. In a highly filled composition, typically with some 1–2 μm calcium carbonate and a great deal of coarse filler, it is, therefore, advantageous also to include a fraction of fine precipitated calcium carbonate. The broad particle size distribution would also favor shear thinning during processing at high shear rates.

Where high filler loading is not appropriate, plastisol thickening is commonly accomplished by low loadings (1–3 phr) of fine-particle silica. Ultrafine fumed silica is the most effective; suitable grades are available as Cab-O-Sil® (Cabot) and Aerosil® (Degussa). Precipitated hydrated silica grades such as HiSil® (PPG) and Zeothix® (Huber) are less effective in building viscosity and are used at higher levels (2–5 phr), but are also less subject to interference by low-molecular-weight additives attracted to their surface. With fumed silica, interaction with viscosity depressants, air release, and foam stabilizing additives can reduce their effectiveness. To minimize this, they are often added to the composition after the other additives have been dispersed; because of the fine particle size of fumed silica, this does not present problems. The typical levels of fumed silica used add very little to opacity or light scattering, again because of the fine particle size, and can be used in translucent compositions. Users should note potential dust hazards with fumed silica.

A number of special purpose thickeners are available. Aluminum distearate (Ferro, Norac), for example, is useful in concrete coatings both as a thickener and bonding agent. At least two organic classes of thickening agent are used where clarity is a consideration. One is polyacrylic acid, available as Carbopol® (Noveon). It is also a useful filler treatment; combinations of filler and polyacrylic acid may cancel each other's thickening effect. Levels of 0.5–3 phr are used. Another is overbased calcium sulfonate, available as Ircogel® 900 from Noveon, also used at 0.5–3 phr. Typically, neither is as effective part-for-part as fumed silica, but both tend to provide greater shelf, temperature, and shear stability as well as clarity.

13.3 ORGANOSOLS

In cases where plasticizer content must be lower than 50 phr to reach a certain set of properties, it may be useful to promote processing by addition of volatile organic additives to form an organosol. Hydrocarbons are most commonly used because of their relatively low materials cost and suitability for solvent recovery operations. In plastisol compounds based on 25–50 phr ester plasticizer, the addition of 5–10 phr of a hydrocarbon diluent will lead to low and stable viscosity. Particular grades should reflect a flash point consistent with safe operations. The rate of evaporation of course decreases with increasing flash point, but the efficiency of solvent recovery increases.

Instead of a hydrocarbon diluent, a ketone or ester may be used instead, in which case it is usually referred to as a dispersant rather than a diluent, reflecting its vinyl compatibility. Typical additives in this class are diisobutyl ketone and hexyl acetate. They have a greater effect on viscosity than hydrocarbons, but require greater investment to achieve solvent recovery. Blends of hydrocarbons with ketones or esters provide cost savings, but not only are they difficult to recover efficiently but it is also difficult to maintain constant composition during recirculation. If suitable solvent recovery systems are not available, the fabricator would be well advised to consider other approaches, such as compounding vinyl latex.

13.4 PLASTISOL PREPARATION

In addition to the effect of shear rate on viscosity, efficient plastisol mixing requires input as to whether problems with dispersion, heat buildup or de-aeration are likely. As with all mixing, it is necessary to break up solid agglomerates (good dispersion) and achieve a homogeneous composition (good distribution). Dispersion requires shear. This input must be supplied without undue heat buildup to avoid the onset of gelation, which can occur easily at temperatures of 40 °C or higher. It is desirable to maintain temperatures below 30 °C with use of a cooling jacket, short cycles, and appropriate agitation speeds.

Mixer agitation should draw the entire contents into the actively mixing section. This is particularly important with plastisols whose viscosity decreases with shear (shear-thinning). In these cases, multiple sets of blades on the shaft are desirable. Shear-thinning compositions usually mix more efficiently at higher speeds, while dilatent (shear-thickening) plastisols tend to respond better to lower speeds.

Low-intensity mixers include ribbon blenders, conical screw mixers, and planetary and double planetary dough mixers. Ribbon blenders and conical screw mixers are used with low- to medium-viscosity compositions where little if any dispersion work is needed, such as for many coating, spraying, and dipping applications. If minor levels of difficult-to-disperse ingredients are needed, such as pigments, they are best added as paste dispersions in plasticizer. Planetary mixers are suited to medium- to high-viscosity plastisols involving low levels of dispersive work but high homogeneity. Typical applications include sealants, adhesives, slush molding, and knife coating of fabrics. Low-intensity mixers generally have cooling jackets, heat development is low, and there is a low tendency to trap air. Batch times, on the other hand, are long, often exceeding one hour if cooling is not available. Planetary mixers such as the Ross^{TM} mixer are suitable also for organosols, since they can be readily connected for solvent recovery of fumes.

High-intensity mixers are of two general types: high speed impellers, such as the Cowles Dissolver^{TM}, and sigma blade mixers, such as the Littleford^{TM} mixer. The Cowles high-intensity mixer should be used with low-viscosity plastisols not requiring significant dispersive work, such as for direct or reverse roll coating, laminating, or spraying. Heat buildup, despite a cooling jacket, and air trapping can be high, so cycles must be short (10–20 min). Sigma blade mixers, on the other hand, are better suited to medium-viscosity plastisols. Heat buildup and air trapping are reduced, at the expense of cycle time. With correct order of addition, sigma blade mixers have good dispersion capability. Both high-speed and sigma blade mixers can be outfitted with fume removal devices for use with organosols.

With low-intensity mixers, typically 60–80 percent of the plasticizer, plus any liquid stabilizer, are charged. After starting cooling water flow and agitation, resin is added at such a rate that it incorporates immediately and is distributed. Powder stabilizers, if used, are then added. This is often followed by a short period of mixing to complete homogeneous resin incorporation. An in-process QC sample may be removed at this point. Filler, with any filler treatment, is then added, again at a rate at which it incorporates as it is added. This is followed by pigment or other paste dispersion. At this point, the rest of the plasticizer is added, vacuum is applied to remove trapped air, and mixing is continued, based on experience of laboratory results. With plastisols of high viscosity, and with unfilled compounds, holding back part of the plasticizer to improve shear is generally not necessary. After mixing is complete, a QC sample is obtained.

With high-intensity mixers, plasticizer is not held back; all liquid ingredients are charged. Under cooling and agitation, resin and then other solids are added to the mixer vortex in a high-speed impeller mixer, or metered into a sigma blade mixer, at which point vacuum can be applied.

The greatest versatility in plastisol preparation is obtained by use of a combination low- and high-intensity mixer, such as the Cowles combination dissolver (Morehouse Industries) or the Ross Versamix$^{\text{TM}}$ combination mixer. These use two or more shafts that can be operated independently. Again, all liquids are charged and the low-speed impeller turned on. The sequence of resin, filler, and other ingredients follows. At this point, high-speed agitation, cooling, and vacuum complete the mix. With low-viscosity compositions, both low- and high-shear impellers may be used from the start. If used with organosols, suitably enclosed motors must be used, as well as fume control devices.

Use of blending resins to reduce viscosity, predispersions of hard-to-disperse ingredients, surface-treated fillers, viscosity depressants, air release agents, and vacuum during mixing can usually be combined so as to provide satisfactory de-aeration. Sometimes, this cannot be done. In such cases, air release can be carried out in a subsequent step; one of the most popular pieces of equipment for such purposes is the Cornell Machine Co. Versator®. This is a combination mixing–vacuum de-aerating device that also improves homogeneity. A number of sizes, including laboratory versions, are available. It might be thought that trapped air might be useful in foamed plastisols; however, this is not the case. Air evolution during foaming leads to pinholes and loss of uniform cell structure.

Plastisols of modest viscosity are commonly filtered through stainless steel mesh to remove tramp contaminants, often from the use of low-cost fillers. For thin-film applications, organosols and low-viscosity plastisols are pressure-filtered through cartridge or bag filters. Organosols may also be refined on three-roll paint mills for improved dispersion and ejection of contaminants.

Plastisols should be stored below 27–30 °C to prevent plasticizer swelling of the resin and build in viscosity. Under proper conditions, viscosity increases for a few days after mixing and then levels off. The level reached depends on the solvating power of the plasticizer, fast-fusing types developing the highest levels. If temperatures in the range of 45–60 °C are reached, gelation will begin, making the product unusable. Proper storage also implies lack of contact with ambient air. Absorption of moisture from the air can destabilize plasticizer viscosity, reduce heat stability of the end product through stabilizer hydrolysis, and negatively affect cell structure in foamed products. A blanket of dry air in the storage tank is helpful; with very sensitive products, dry nitrogen has been used.

CHAPTER 14

Formulating Expanded Products

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14.1 INTRODUCTION

In PVC articles of all types, foamed or expanded products offer the advantages of cost and weight reduction. With rigid PVC products, foamed structures also add technical advantages of thermal insulation, machinability, and often attractive appearance. With flexible products, cost and weight advantages are combined with increased resilience, surface texture, improved sealing characteristics, thermal and sound insulation value, and provision of flotation, providing products not available with other technology. Foamed PVC production began in the mid-20th century using methods previously devised for dry rubber and latex, and for polyolefins. For example, plastisols or PVC latex were mixed with carbon dioxide at 30 atm pressure in

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specialized equipment as would used for rubber latex.[1] This process is referred to as physical foaming or elastomeric foaming, and is now rarely used. The introduction of carbon dioxide under pressure into rigid PVC is, however, now of great interest. Static systems in which carbon dioxide is forced into PVC in a closed reactor have been described by Kumar and co-workers.[2] Microcellular foams of density decreasing monotonically with temperature in the range of 55–105 °C were obtained with 4.8 MPa carbon dioxide. Injection of carbon dioxide and of argon during extrusion of rigid PVC has been studied by Dey and co-workers.[3] It will be interesting to note the commercial development of this process, which has the potential of rendering blowing agent technology obsolete. The physical foaming of plastisols by mechanical agitation will be discussed in a following section.

Most PVC expanded products result from the use of chemical blowing agents. The choice is limited by the requirements that the additive be effective in a desired and controlled processing temperature range and time frame, otherwise stable, nontoxic, colorless, nonstaining, odorless, cost-effective, inert as regards processing stability and service life, readily dispersed, useful at low loadings, not overly exothermic in decomposition, and not a generator of undesirable residues. There are, of course, no ideal chemical blowing agents, only useful compromises. (Since the ideal additive would be no blowing agent, this reinforces interest in inert gas injection during processing.)

The first widely used chemical blowing agent was sodium bicarbonate. The rate of decomposition to carbon dioxide can be controlled by temperature and pH. Cell structure is variable, typically with considerable open cell character (individual cells being open to each other). The generation of carbon dioxide is endothermic and thus not a PVC stabilization problem, bicarbonates actually being secondary stabilizers. The additive, even when stearate-coated for improved dispersion in polymers, is very inexpensive. Poor cell structure and open cell character have, nevertheless, greatly limited use in flexible PVC compounds. The development of rigid PVC foam core products has provided new opportunities for bicarbonate blowing agents, often in concert with organic additives, and will be discussed later in Section 14.7.

14.2 ORGANIC BLOWING AGENTS

The most widely used blowing agent in PVC (and other polymers) is azodicarbonamide, NH_2—CO—N=N—CO—NH_2, known generically as AZO (CAS 123-77-3), a yellow powder, specific gravity 1.65. AZO decomposes exothermally to a mixture of nitrogen, carbon monoxide, and minor amounts of ammonia and other nitrogenous gaseous products, leaving a residue of distinct odor comprised of urazole, biuret, cyanuric acid, urea and ammonium salts. The related half-acid, NH_2—CO—N=N—CO—OH, is unstable and decomposes spontaneously. Therefore, any additive that promotes amide hydrolysis will activate AZO decomposition. This is fortunate, because the decomposition temperature without activation, 200–210 °C, is generally too high to be useful. The proportions of gaseous products and residue components vary somewhat with the activation used, as does the gas yield. The latter is typically about 200 ml/g. Activation is the key to organic blowing agent control and, therefore, widespread use. For example, a useful research project would be to find suitable activators for the now widely available airbag inflator, 5-phenyltetrazole (decomposes 215 °C), which yields nitrogen with an odorless residue. Useful activators for AZO include zinc oxide, urea, zinc stearate, and zinc-based stabilizers generally (all strong); barium, calcium, lead, and organotin stabilizers (moderate); calcium oxide, and adipic, benzoic, citric, and salicylic acids (relatively weak). Strong activators are active in the range of 150 °C; moderate, around 170 °C; weak, around 180–185 °C.

A blowing agent less widely used in PVC is *p,p′*-oxybis(benzenesulfonhydrazide), OBSH, $H_2N—NH—SO_2—C_6H_4—O—C_6H_4—SO_2—NH—NH_2$ (CAS 80-51-3). OBSH decomposes at 150–160 °C. It is activated strongly by urea and triethanolamine, with decomposition in the range of 125–135 °C. As is also the case with AZO, nitrogenous activators are rarely used in PVC. Lead-, tin-, and cadmium-based stabilizers are moderate activators, as is calcium stearate. Zinc compounds are poor activators for OBSH, and calcium oxide is a retarder. Thus, whereas AZO responds to acid–base catalysts generally, OBSH is activated by nucleophilic displacement. OBSH is about twice the cost of AZO on a per-pound basis, closer to three times the cost on a gas-yield basis.

Combinations of AZO and OBSH are used, but must be evaluated carefully, since OBSH also activates AZO.[4] Activation of OBSH and AZO has been discussed in detail by Rowland.[5] Much of the data is also presented in the Chemtura Bulletin, Chemical Activators for Celogen® AZ. OBSH is of specific gravity 1.43 and has a gas yield of about 125 ml/g, comprising nitrogen and water vapor, leaving a polymeric residue of very low odor. This has led to its investigation as a replacement for AZO in automotive components such as extruded flexible sealing strips and in foamed upholstery. AZO and OBSH should be handled with care, since both are readily ignited and are considered air and water pollutants by various regulatory authorities.

A blowing agent sometimes used in plastisols is dinitrosopentamethylene tetramine (DNPT), specific gravity 1.45, having a lower per-pound cost than AZO and a higher gas yield, about 250 ml/g, comprising nitrogen, ammonia and formaldehyde, leaving an amine-containing residue with an uningratiating odor. Although decomposing without activation at 200–205 °C, activation with urea, melamine, glycols, or lead stabilizers yields foam formation at 150–165 °C. At one time, AZO and DNPT blends were used in flooring plastisols, particularly vinyl asbestos compositions using melamine also as a stabilizer; they are co-activating and enable close control over foam yield and structure. DNPT is available from KumYang as Cellcom® A, Dong Jin as Unicel® ND, Eiwa as DPT, and Chemtura as Opex® 80, and may still find use in some parts of the world. It tends to produce closed cell foam when activated with urea, and open cell foam with boric acid/urea combinations. Both are typically stabilized with dibasic lead phosphite. DNPT is highly flammable and difficult to extinguish once ignited. As an *N*-nitroso compound, it is possibly carcinogenic, although this has not yet been supported by animal data. These factors have led to its gradual discontinuance in rubber and plastics in Europe and North America, despite the cost advantage.

14.3 CHEMICAL BLOWING AGENT GRADES

There is more experience and technology associated with AZO than with any other chemical blowing agent. Grades with an average particle size ranging from 1.5 to 12 μm are available under the trade names Cellcom® AC (KumYang), Celogen® AZ (Chemtura), Kempore® (PolyOne), Vinylfor® (Eiwa), Azobul® (Arkema), AZTF (Sovereign), Unicel® D (DongJin), Porofor® ADC, Genitron®, and Ficel® AC (all Lanxess), and others. Although the decomposition of pure AZO drops only a few degrees in going from 12 to 1.5 μm, activated grades show great decreases in decomposition temperature as particle size decreases. This is generally taken as reflecting an increased availability for activation as surface area increases. Most vinyl applications use grades of AZO having an average particle size of 2–5 μm. In grades recommended for vinyl, dispersability is often increased by addition of a low loading (2–3 percent) of fine-particle silica. This also reduces plateout, which can otherwise be a problem with AZO in extrusion and injection molding. Easily dispersable grades are often stearate-coated, also lowering dusting. In non-activated grades, this is typically calcium stearate. In activated grades decomposing at lower temperatures, AZO is coated with zinc stearate. This tends to reduce yellowing associated with AZO usage, and is promoted as reducing the level of titanium dioxide needed to compensate. DNPT and AZO/DNPT blends for vinyl, such as Cellcom® ACP/W, have similar coatings.

OBSH is available in 5 and 3 μm grades, the latter typically for automotive use, from KumYang (OBSH), Chemtura (Celogen® OT), Eiwa (OBSH), DongJin (Unicel® OH), Lanxess (Porofor® RTM), and others. Generally, activation is not required in vinyl. Discoloration and plateout are typically not problems, and the residue has little or no odor. More widespread use of OBSH in vinyl has been limited mainly by cost considerations. Use of AZO, DNPT, and OBSH in a variety of plastics and elastomers is presented in the KumYang company bulletin, Blowing Agents.

Sodium bicarbonate (CAS 144-55-8), coated for ease of dispersion, is available from many suppliers and distributors, such as Genitron® TPBCH from Lanxess. A typical gas yield is about 165 ml/g at 160–210 °C, lower temperatures reflecting acid pH, higher reflecting neutral or alkaline. Activation can be carried out with citric acid or surface-treated urea, such as Cellex® (KumYang) or BIK-OT® (Chemtura). Citric acid tends to improve both color and gas yield. The cost advantage of using sodium bicarbonate or combinations with citric acid is such that these are considered whenever a more or less open cell structure can be tolerated, such as when the foam layer is covered by a solid vinyl skin as in foam core constructions. Sodium bicarbonate/AZO combinations are also widely used in such applications.

14.4 INCORPORATION OF BLOWING AGENTS

Efficient use and uniform cell structure depend on good distribution of blowing agent in the compound. With coated grades, there is little tendency for particle agglomeration, thus avoiding the need for dispersive shear. High-shear mixing must be avoided to prevent decomposition from microheating. The use of high-shear paint mills to produce paste dispersions of blowing agents has led to accidents from ignition. Liquid or paste dispersions, such as 50 percent AZO in plasticizer, should be run in a Henschel or similar mixer and then filtered to remove undispersed material, rather than run on a high-speed three-roll mill. Low-shear three-roll mills can also be used. Such products are useful for introduction of unmodified blowing agents into plastisols or solution coatings and are available commercially, for example, 3684B (50 percent AZO in DINP), 3761B (50 percent AZO in DIDP), and 3563B (50 percent activated AZO in DINP) from VitaPlas; Kenmix® (50 percent AZO/DOP) from Kenrich; and the Ficel® HF liquid series from Lanxess. Coated dispersible grades may be added directly to the plastisol mixer, in which case it is advisable to screen the final product, for example, through 200 mesh.

In rigid vinyl compounding, polymer-bound blowing agents in pellet form can be used with pelletized processing. Such products are available, for example, from Lanxess, the Ficel® HC organic blowing agent series, Ficel® DP sodium bicarbonate, and VPKA 9175 combination. With dry-blend compounding, a liquid dispersion can be added, providing a dust-free process. This is preferable to low-shear tumbling of the resin with blowing agent and traces of plasticizer (0.5 percent) to adhere the additive to the resin granule. Heat stabilizer dispersion is also very important, since organotin and other stabilizers activate AZO, and calcium stearate serves as a nucleating agent both for AZO and sodium bicarbonate, influencing cell structure and foaming time.[6] Thus, simultaneous addition of liquid stabilizer and blowing agent should be approached with caution; it is usually preferable to add the stabilizer to the resin and a dispersion of the blowing agent later in the cycle.

14.5 FOAMED PLASTISOLS

Plastisols form the most commercially significant class of foamed plasticized vinyl products. In development of plastisol-based foam, the blowing agent–activator system generates gas as, or shortly after, fusion is completed; that is, at temperatures above the fusion temperature of the specific compound. Fusion, not merely gelation to a dry appearance, is needed to constrain the gas produced. At a given temperature above the decomposition point, gas evolution is typically linear with time until most of the expansion has occurred, then levels off. Thus, increasing oven residence time after fusion will increase gas evolution to a point near the maximum available from the loading of blowing agent, and then will have little or no further effect. Increasing the level of blowing agent tends to increase the rate as well as the volume of gas evolution. Increasing the level of activator will increase the rate of gas generation, up to a point, but not the total volume; occasionally, volume may be slightly decreased. Increasing the oven temperature will increase the rate of gas generation, and may provide a slight increase in volume from decreased incidence of side reactions. With all chemical blowing agents, the rate of gas generation increases with decreasing particle size.

These relationships are often described in terms of the expansion factor (EF), the ratio of foamed to applied thickness. Commonly foam density = unfoamed density/EF is used instead. In plastisols, AZO is typically used at 2–5 parts per 100 of resin (phr). When zinc oxide is used as an activator, it is often at 0.3–1.0 phr, or may be included in a powder mixed metal stabilizer. Liquid zinc-based activators, for example, Akrostab® M-823 (Akcros), are used at 0.5–1.0 phr, or may be part of another liquid mixed metal stabilizer. Examples are given in Chapter 4. Stabilizers used with activated grades of blowing agents should be evaluated thoroughly for potential interaction on heat aging. Resin selection for plastisols is covered in Chapter 2, and plastisol technology in Chapter 13.

The extent of expansion possible is limited by the level of plasticizer. Expansion factors of 4 or greater typically require at least 55 phr of plasticizer, depending on the viscosity of the compound during and after fusion at oven temperatures (commonly in the range of 190 °C). As plasticizer level is decreased, the activity of the blowing agent–activator system should be increased in compensation. With slower-fusing, less-volatile plasticizers such as DINP and DIDP, it may be necessary, on the other hand, to decrease activation and run at higher oven temperatures. Generally, performance properties govern plasticizer selection and level, and blowing agent–activator systems are adjusted to fit these needs.

Calcium carbonate is the most widely used filler in foamed plastisols, typically in the range of 10–30 phr. The higher end of the range can reduce set from indentation; loadings above 30–40 phr tend to interfere with development of uniform cell structure. Antioxidants with a tendency to discolor, such as BHT and bisphenol A, should not be used with nitrogenous blowing agents, particularly with AZO and DNPT. Suitable modern hindered phenolic antioxidants are described in Chapter 4. (Antioxidants with colored oxidation products should no longer be used in vinyl compounds of any description.) Plastisol viscosity depressants should be checked for blowing agent activator interactions, as should air release additives, although the latter will often improve foam quality.

Chemical blowing agents enable the plastisol to be dried to a gelation state without fusion and gas production. In this state, the product can be printed or decorated—for example, printed in certain areas with a coating containing inhibitors that react with and deactivate the activator, leading, after expansion, to embossed areas with very much less expansion when gas formation is carried out at a temperature requiring activation. In another application, a second blowing agent can be used that decomposes at gelation temperature, the primary system decomposing during fusion. This leads to small voids being formed during gelation (from the lower-temperature blowing agent). These expand during fusion, leading to a textured effect. Such combinations can be achieved with AZO and OBTS blends having activation favoring low-temperature OBTS decomposition but not AZO activation. Similar schemes were used in the past with AZO and DNPT blends. Another possibility is to include a low-temperature blowing agent for decomposition during gelation. One candidate is *p*-toluenesulfonylhydrazide (TSH), specific gravity 1.42, which decomposes at about 150 °C with a gas yield of about 115 ml/g. The product does not generate color or odor; it is available as Cellcom® H (KumYang), Celogen® TSH

(Chemtura), Unicel® H (DongJin), and others. TSH is less expensive than OBTS, but more so than AZO or DNPT.

Foamed plastisols are usually blown in a high-air-velocity oven for most efficient heat transfer with degree of expansion controlled both by temperature and dwell time. Once blowing agent decomposition is complete, the product should exit immediately. No further expansion will occur, but degradation and loss of cell structure may (as well as output rate).

14.6 FOAMED PLASTISOL APPLICATIONS

14.6.1 Coated Fabrics

With vinyl-coated fabrics, foam structure provides products much like leather in feel and appearance. The term "leathercloth" was devised by suppliers offended by the designation as artificial or synthetic leather. (Vinyl technologists sometimes refer to leather as imitation vinyl.) The construction generally comprises a fabric backing coated with a foam layer and overcoated with a solid wear layer. The choice of fabric determines strength and the coated layers provide the feel and wear properties of the product.

When coating directly onto fabric, it is often useful to saturate or prime the fabric with a solid plastisol to prevent the fabric structure from showing through the foam and wear layers. This can be the same formulation as the foam layer, minus the blowing agent/activator system, but typically with a bonding agent for increased fabric adhesion. The fabrics most often used are polyesters. The bonding agents are usually plastisol-compatible thermosetting urethane systems, such as Vulcabond® MDX (Akzo Nobel), used at 2–5 phr. The fabric is generally also primed before transfer instead of spread coating. In this technique, the plastisol layer or layers are coated onto a smooth-release paper liner or onto a continuous belt, and the fabric is then laminated. This broadens the range of fabrics that can be used; they need not be tightly woven or even woven at all. Use of release liners requires lower initial investment than a continuous belt, but with a limited liner lifetime.

Plastisol-coated polyester fabric foamed to provide texture is often used as a printable background for computer-generated signs and displays. An example is Artex® Canvas from Ultraflex Systems.

Coatings for luggage exteriors must be durable. Typical compounds use 50–70 phr of DINP or DIDP, 10–20 phr calcium carbonate filler, colorants as required, 2–3 phr 5–7 μm AZO, and 2–3 phr of a liquid activator–stabilizer. In almost all applications, DOP has been replaced with plasticizers of lower volatility. This is particularly true of automotive upholstery. DIDP blends with trimellitate plasticizers have become common; use levels are typically about 80 phr, with 5–10 phr calcium carbonate, colorants as needed, 2–3 phr of 3 μm AZO, and 2–3 phr of activator–stabilizer. Lower residual odor is achieved with 3–5 phr 3 μm OBSH instead.

Temperature-sensitive fabrics such as polypropylene can be coated with foam plastisols based on vinyl copolymers, with use of activation systems enabling AZO decomposition at 150–160 °C (strong activators listed in the foregoing). Strongly activated AZO products that decompose in this range are commercially available, for example, Cellcom® PLC (KumYang) and Ficel® LE (Lanxess). Alternatively, TSH could be used, particularly in the interest of low residual odor. Examples of TSH commercially available are listed in the foregoing.

14.6.2 Flooring Components

Mechanically Embossed Flooring In this process, referred to as gravure or rotogravure flooring, foamable plastisol containing 3–5 μm AZO is coated onto a backing and oven-gelled, but not fused and blown. This coating is then printed with the desired pattern, usually of 0.3–0.6 mil (8–15 μm) thickness, by the rotogravure process, and then top-coated with a clear plastisol. Passage of the composite through an oven at elevated temperature causes fusion of both layers and expansion of the foam layer. It is then embossed mechanically while hot, using an engraved embossing roll, which, if desired, can be synchronized to the printed pattern. With ingenuity in printing and, to some extent, in blowing agent level, a variety of patterns can be produced with only a few gravure and embossing rolls. Nevertheless, the process tends to generate flooring having a degree of sameness—often inconsistent with marketing campaigns.

Chemically Embossed Flooring In this process, also referred to as gravure or rotogravure flooring, the foamable plastisol is again coated onto a backing, gelled, and printed. In this case, it is overprinted where desired with ink containing an inhibitor for the activator, which is usually zinc-based. Fumaric acid and trimellitic anhydride have been used to complex zinc activators, but the sharpest definition is with benzotriazole and substituted benzotriazoles.[7] These complex and deactivate zinc oxide and other zinc compounds, and also tend not to migrate out of the print in which they are applied into neighboring areas. When this occurs, the embossing (from decreased blowing agent decomposition) becomes blurred. Since not all of the blowing agent, usually 2–3 phr 3 μm AZO, is consumed, typically 2–5 phr of titanium dioxide is added to counter any tendency for discoloration. Several blowing agent suppliers offer AZO plus zinc activator grades predispersed in plasticizer for this application. After the complex printing process, the foamable layer is again top-coated with clear plastisol, and the composite is expanded, leading to expansion to a much greater extent in the areas not overprinted with inhibitor. The ratio of activator to inhibitor used can produce a variety of effects. Since OBSH is generally used without activation in vinyl, it has had little use in chemically embossed flooring. Since activators such as urea or melamine could be complexed, for example, with benzoic acid, its use is a possibility.

Screen Printed Flooring In this process, foamable plastisol inks are applied to the backing through hollow cylindrical mesh screens. Parts of each screen can be blocked to achieve a pattern. In this case 5–6 mil (0.13–0.15 mm) thicknesses are printed—far greater than with gravure printing. Although a number of printing stations can be used, each requires an oven zone to gel the screen coating ahead of the next printing head. A textured surface can be produced in more than one way. The inks used to form the pattern can contain different levels of blowing agent. After a clear plastisol topcoat is applied, the composite is passed through a hot oven and all blowing agent decomposed, yielding a product with depth. Alternatively, patterns can be printed onto a pregelled sheet containing blowing agent, with some or all of the pattern inks containing activation inhibitor, this time at a low level because of the thickness printed.

Although rotogravure flooring requires a higher level of investment than screen printing, its being adaptable to widths as great as 12 ft (3.7 m) has led to increasing acceptance. There is continued experimentation with replacement of plastisol coating with calendered expandable films. Although close processing control and a high level of investment are required, high output forms an attractive target.

14.6.3 Wall Coverings

Vinyl-coated products now dominate the wall covering market because of the balance of properties, such as strength, durability, and ease of cleaning, versus cost. Foamed layers reduce cost and weight, as well as adding to appearance. Screen printing is more widely used than gravure techniques, since narrower widths are required as compared with flooring. Chemical embossing using AZO inhibitors is common. In addition, it is also carried out by printing with inks containing activator onto gelled plastisol with unactivated blowing agent, usually AZO. Mechanical embossing is also used, to produce either a random texture or one registered with the pattern. Special texture effects are obtained with combinations of blowing agents, either AZO and OBSH or unactivated AZO and an integrally activated grade. With the latter, chemical embossing is more readily achieved. Because of the lower mass as compared with flooring, higher line speeds are reached. A factor favoring this is that cell structure is less important because of the lower incidence of impact, indentation, and wear.

Similar mechanically embossed products, using woven or nonwoven backings (often cotton), but lacking printed patterns are used as backgrounds for displays and signs. An example is Wallscapes® Plus from Ultraflex Systems. Grades of wall coverings are given in ASTM E 84. Some are now produced by calendering expandable flexible vinyl film onto a woven or nonwoven backing. This requires close processing control to avoid premature blowing agent decomposition; low levels of activation are used with AZO. The process has the attraction of widths up to 12 ft (3.7 m) at high output.

14.6.4 Vinyl Foam Tape

Expanded vinyl has been used as a pressure-sensitive tape backing for many years. Typically, a low-density foam is plastisol-coated on a casting liner that is used a number of times, or onto a continuous belt. After fusion and expansion, one or both sides are transfer-coated with adhesive that has been dried (and sometimes thermoset) on a liner. The adhesives used are generally polyethers, acrylates, or thermosetting acrylates, all of which adhere well to vinyl. Both single and double adhesive-coated low-density vinyl foam tapes are widely used as seals in construction. Typically, they simply take up space, preventing influx of air or sound. Formulations use about 100 phr of plasticizer (either DOP or DIDP depending on service requirements), with 6–9 phr of 3 μm AZO to reach densities as low as 0.1 g/ml. Double-coated harder foams are used for mounting tapes, often with a thermosetting adhesive and with the foam primed with a urethane coating to block plasticizer migration. Such tapes have been used with less than total success in replacing mechanical attachments to hold decorative trim and emblems to automotive body exteriors. In this and other applications, vinyl foam competes with polyurethane products.

14.6.5 Miscellaneous Plastisol Foam Applications

Bottle Cap Liners Most bottle cap liners use triple-layer EVA extrusions—dual extruders feeding a single head with clear EVA for the top and bottom layers and EVA containing blowing agent for the center. Fine-particle activated AZO is used, such as Cellcom® JTR (KumYang), decomposing at 150–160 °C. Blowing occurs as the product exits the die as a sheet, which is then die-cut. Trim can be recycled at low levels. EVA has insufficient oil resistance for a number of products, edible and otherwise. In such cases, foamed plastisols are common, generally using 1–2 phr 3 μm AZO, limited to 2 percent in food contact applications. Activation is usually by means of food-grade zinc oxide or stearate, 0.1–0.3 phr. FDA regulations are given in 21CFR 175.300 and 177.1210.

Automotive Sealants In filling underbody dead spaces, foamed plastisols compete with urethanes and other products. Such plastisols are highly filled, often with over 100 phr calcium carbonate, and plasticizer levels of 100–140 phr. Adhesion promoters for metal bonding (Chapter 12) are used with 2–4 phr of 5–7 μm AZO, yielding expansion factors of 1.5–2.

Molded Vinyl Foam With other materials such as urethanes and elastomers, most foam products are molded. They are either allowed to expand under low pressure to fill the mold, yielding an open cell structure, often with a skin (as in, e.g., crutch pads) or molded and thermoset under pressure and subsequently expanded in an oven, yielding a closed cell structure (as with foam rubber shoe soles or mattress components). The products of oven expansion, referred to as “buns,” can be skived and die cut to gaskets or seals. The latter process is also carried out with vinyl. Molds are filled with plastisol, fused and cooled under pressure, and then expanded in an oven at 100–120 °C, softening the polymer and enabling the trapped gas to expand. For highly defined shapes, this step can be carried out in a second mold.

Typically, fine-particle AZO is used with zinc oxide or zinc carboxylate activator. Titanium dioxide is often used to reduce color with AZO loadings above 2 phr. Proprietary low-discoloring grades of AZO are available, such as Cellcom® AC5000FX (KumYang). Applications include moldings for insulation, buoyancy, and shock and vibration absorption. Molded products not from plastisols, such as vinyl foam footware components, are discussed in Chapter 21.

14.7 FOAM CORE PIPE

Foam core pipe provides cost and weight reduction in low-pressure (DWV) applications, the weight decrease also facilitating installation. These advantages tend to outweigh increased investment in equipment, and generally lower line speeds than with solid pipe. Nevertheless, solid vinyl DWV pipe remains the most prevalent product. Most foam core pipe is extruded using the free expansion or free foaming process, where the extrudate expands on leaving the die face and, after a set length of air travel, reaches a cooled calibration tube that sets the final dimensions. The head and die is fed by a second extruder providing a solid skin layer. Suitable co-extruders are supplied by Krauss-Maffei, Chase Machinery, Battenfeld, and American Maplan. Typical formulations are given in Section 4.2.3. Most rigid vinyl extrusions using free expansion are based on 3–5 μm AZO at 0.2–0.4 phr with moderate activation by the organotin or, in some parts of the world, lead stabilizer. With barrel temperatures of 180–190 °C, and the head and die at 190–200 °C, output and expansion with AZO is rapid. With ingenuity, comparable rates might be achieved with calcium/zinc/costabilizer systems, which have been advertised, but reports of results have not been forthcoming. Foam core extrusion systems have been reviewed by Patterson and Szamborski[8] and by Schipper et al.[6]

Alternatively, foam core pipe can be extruded using the controlled expansion or inward expansion process, also known as the Celuka™ process.[9] In this process, the cooled calibration tube that establishes outer diameter is mounted on the die. The expansion is, therefore, inward and a heavy skin layer is formed, sometimes eliminating the need for a second extruder. It is also feasible to run to lower densities with this process (0.35 g/ml), and large diameters can be accommodated. A further advantage is that it is possible to use sodium bicarbonate or blends with AZO, lowering material cost. The foam density and cell structure of such blends have been studied by Thomas and Harvey.[10] Foam core DWV pipe is supplied in diameters from 1.5 to 12 in (3.8–30.5 cm) by, among others, Genova, Charlotte Pipe, Bristolpipe, Ipex, and Cresline. A typical 6 mm wall will have 3.5 mm foam core between 1.2–1.3 mm skin layers, the latter having a density of about 1.5 g/ml and the foam layer a density of about 0.65 g/ml. Such pipe is described in ASTM F 891 and sanctioned in National Sanitation Foundation (NSF) Standard 14. Larger-diameter foam core pipe can be produced using ABS instead of vinyl.

14.8 FOAMED BUILDING PRODUCTS

Vinyl Siding Foamed siding panels have been extruded by both the inward expansion and free expansion processes. The products are 5–6 times thicker than solid vinyl siding, with densities of 0.5–0.6 g/ml, compared with 1.45–1.49 g/ml for solid vinyl. The advantages include improved thermal insulation, and reduced thermal expansion and contraction, leading to much lower tendency to distort, good resistance to wind damage, and greatly improved handling, permitting easy sawing and attachment with hammer and nails. The last notably facilitates home repair. The subject has been reviewed by Szamborski and Butterbaugh.[11] Foam core siding has had considerable success in Europe with simple board panels. The lack of market penetration in North America reflects the cost of the process, not so much in terms of equipment investment, but rather line speed—a reflection of the prodigious output of solid vinyl siding routinely achieved. The latter derives from extrusion of a flat solid sheet at high speed, followed by thermoforming and trimming to various complex siding configurations. This would be difficult with an expanded construction; it would be most easily approached by lamination of foam to thermoformed siding. This is being done, but not as yet with vinyl foam. Alcoa, for example, offers insulated solid vinyl siding backed with polypropylene foam, and CertainTeed supplies Cedar Boards®, solid vinyl siding backed with expanded polystyrene.

Profile Extrusions Foam core profiles with solid skin are co-extruded for use in window components, in woodgrained moldings for use with paneling, and in window blinds, and as a wood replacement in miscellaneous applications such as picture frames. A variety of the last item is manufactured by, among others, Marley Moulding of Virginia. Depending on the application, compounds for foam core extrusion may contain impact modifiers, and will contain polymeric processing aids as well as a balance between calcium stearate and paraffin wax, since these factors affect cell formation and product appearance as well as output. Starting formulations are given in Section 4.2.3. Extrusion conditions have been studied by Rabinovitch and co-workers.[12] Their conclusions are that there is an optimum temperature range for formation of smooth, void-free, uniform cell formation, in the range of 190–196 °C, at relatively low screw speed. At excessive screw speeds, the window of processability is reduced or eliminated by shear heating.

Typically, the inward foaming process is used for high output of boards or large moldings of similar shape, using twin-screw extrusion and AZO–sodium bicarbonate combinations. Smaller profiles are coextruded using dual single-screw extruders with L/D ratios of 20–25/1 and compression ratios of 2–2.5/1 using stabilizer-activated AZO in free expansion. If an absolutely smooth surface is not necessary, such as if texture is desired, co-extrusion of a skin layer is omitted. With the inward foaming process, a smooth surface usually results without a skin layer being added. With both, the die cross-section should decrease uniformly to the exit point so that melt pressure is able to contain the gas. Die lands are short. The calibration cooling unit must be longer than with solid compounds because of much lower thermal conductivity, or followed by a second cooling unit. During extrusion, plastication must occur rapidly at relatively low temperatures to prevent back escape of gas through the feed hopper. Thus, a 157–165–176–193–185 °C profile on a five-stage barrel, with the die at 185 °C, $L/D = 24/1$, and a compression ratio of 2.5/1, on a 2.5 in (6.4 cm) extruder with tin-stabilized compounds containing 0.5 phr 5 μm AZO is recommended the KumYang Company in their bulletin, Blowing Agents.

Extruded Sheet Sheet is also extruded using both free and inward expansion processes. In the former case, a solid skin may be co-extruded. Formulating for both has been reviewed by Szamborski and Pfennig.[13] Free-foaming compounds using 0.5–0.65 phr 3–5 μm AZO, 4–5 phr calcium carbonate filler, 1–3 phr titanium dioxide, and standard organotin/calcium stearate/paraffin wax combinations were evaluated with acrylic processing modifier up to 8 phr. Addition of acrylic impact modifier to such systems converted impact failure from brittle to ductile; that is, it notably improved elongation under rapidly applied load. ABS and CPE modification have also been suggested in the KumYang bulletin, Blowing Agents. Inward foaming (Celuka) sheet often uses about 2 phr sodium bicarbonate instead of AZO, or 1–2 phr plus 0.5–1.0 phr AZO.

Properties of rigid vinyl foam versus density has been reviewed by Patterson.[14] Tensile and flexural strength and modulus drop sharply at densities between 1.4 and 0.7 g/ml, then slowly drop. Impact strength drops immediately to low values unless failure is converted to ductile distortion with addition of impact modifier. Calcium carbonate filler had very little effect on tensile or flexural modulus at densities below 0.7 g/ml. This suggests the possibility of improvement with fillers of higher aspect ratio. This would be of interest in applications such as display and advertising panels, for which foamed vinyl is highly suitable, being readily printed and decorated, with reasonably good service life.

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CHAPTER 15

Alloys and Blends

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15.1 INTRODUCTION

Polymer blends and mixtures are often referred to as "polyblends" and sometimes as "alloys," a term borrowed from metallurgy. Commonly, "alloy" is used to designate a blend of polymers having at least some properties that are more useful than what would be expected from weight-averaging those of the individual components. For example, a blend of natural rubber with EPDM will be found to have better ozone resistance than one might anticipate from the exceedingly poor ozone resistance of natural rubber. These polymers are "compatible"; that is, their blends seem visually homogeneous on a macroscopic scale. Few blends employ polymers that are "miscible" (i.e., mutually soluble). In the above example, it can be determined that, on a microscopic scale, natural rubber and EPDM have largely separate domains. The effect of this—the protection of the natural rubber phase by an EPDM phase—is

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what provides unanticipated ozone resistance. Similarly, impact modifiers are compatible, but not miscible with PVC, and this underlies their beneficial action.

15.2 PVC/NBR COMPOUNDS

Acrylonitrile–butadiene rubber (NBR) is the elastomer used most often to modify the properties of PVC. Almost all grades of NBR are compatible, but not miscible with PVC. The set of properties that are achieved are sufficiently impressive that many technologists consider such blends to be alloys. Compared with flexible PVC compounds in general, NBR addition provides increased elastomeric behavior and feel, improved oil and solvent resistance, tear strength, abrasion resistance, flex resistance, improved compression set, and resistance to migration and to volatile loss. Compared with pure NBR, such compounds often have excellent processing in extrusion, molding, and calendering applications, and can provide improved cell structure, color retention, and weathering stability. Thus, these blends can compete with Neoprene and Hypalon® compounds in applications such as cable jackets and hose covers. This technology has been used for many years. At one time, the availability of NBR only in bale form restricted its use to internal mixers or to users equipped to grind bales of rubber. NBR is now available in fine powder grades suitable for dry-blend operations, with or without subsequent pelletizing.

15.2.1 NBR Grade Selection

The characteristics considered in selecting a particular NBR grade include viscosity (average molecular weight), gel content, particle size, and acrylonitrile content. Elastomer viscosity is typically measured at low shear rates using a Mooney viscometer per ASTM D 1646, with which the back torque is measured as a rotor shears the sample, usually at 100°C. Generally a 1 minute hold at temperature is followed by measurement after 4 minutes' shear, leading to a value referred to as ML100 $(1 + 4)$. Low-viscosity grades, such as for injection molding, are in the range of ML100 $(1 + 4) = 20$–40 units; medium viscosity, such as for extrusion, 40–60; high viscosity, such as for hot calendering, 60–100 units. These are apparent viscosities, and are highly dependent on equipment geometry and state of equipment wear, and suitable only for comparisons.

Gel content in NBR is useful in limiting die swell and shrinkage in extrusion. With substantial NBR content, compounds are extruded like rubber—more or less on size and not drawn down. Minor gel content may also assist calendering and molding, but is not useful in coating applications. PVC gels, on the other hand, are not useful in PVC/NBR blends; they inhibit poor dispersion, and should be minimized. In dry-blend operations, particle size less than 1 mm is recommended for uniform distribution, particularly in low-shear operations. With compounds fluxed in an internal mixer, particle size is less significant.

Most commonly, NBR polymers of medium acrylonitrile (ACN) content (33–35 percent) are used. These are compatible in all proportions with PVC. In plasticized blends where low-temperature flexibility is required, this is usually accomplished with choice of plasticizer, rather than by use of NBR with lower ACN content. At high NBR levels, improved low-temperature flexibility can be gained by use of 28 percent ACN grades. For injection molding, occasionally 38–40 percent ACN grades are used. High ACN levels increase flow during processing, but detract from low-temperature flexibility. For maximum abrasion resistance, carboxylated NBR (butadiene/acrylonitrile/acrylic acid) can be used instead. Prevention of re-agglomeration of NBR powder requires the use of a partitioning agent—originally calcium carbonate or talc, but now more commonly for blending PVC powder. The levels used are, in some cases, high enough (5–10 percent) that they must be considered in formulation.

There has been considerable consolidation in NBR supply in recent years. Powdered medium ACN grades for PVC supplied worldwide by Zeon Chemicals include Nipol® 1492P80 (70–85 Mooney) and the partially crosslinked 1411, both partitioned with talc. Crumb grades for internal mixing include 1442 (75–90 Mooney, talc), 1432T (75–90 Mooney, solution PVC), and the carboxylated 1472HV (35–50 Mooney, talc). Grades with higher ACN levels are also available.

Grades supplied worldwide by Lanxness (formerly Bayer) include Baymod® N 34.52 (45 Mooney) and N 34.82 (70 Mooney), both partitioned with calcium carbonate. New grades include N VP KA 8945 (50 Mooney, PVC) and N VP KA 8641 (115 Mooney, calcium carbonate). Polimeri Europa (formerly Enichem) supplies Europrene® N 33.45P (40–50 Mooney, PVC), N33.70P (also PVC-coated) and N33.80P (filler-coated), as well as the crumb grades N33.70G and N33.80G (both filler-coated).

INSA of Altamira, Mexico, distributed by ParaTec Elastomers, supplies powder grades Paracril® BJLT M50 (50 Mooney, 9 percent talc) and 33L80 (80 Mooney, 15 percent calcium carbonate). Crosslinked grades include 32.55XL (50–60 Mooney) and 33.55XL (55 Mooney). Both are partitioned with 9–10 percent PVC. In addition, Paracril® 33L80 and a grade of crosslinked 33.55XL are supplied partitioned with calcium carbonate. Powder grades are available from the Indian suppliers Milin Corporation and Apar Industries. A crosslinked grade, Seetec® P8300XL, is available from Hyundai.

Nitriflex of Brazil, distributed by Harwick Standard, supplies a range of powdered NBR products based on Goodyear Chemigum® technology. The NP 2100 series includes 38 Mooney (NP2183) and 68 Mooney (NP2174), coated with 12 percent PVC, and 47 Mooney (NP2021), coated with 12 percent calcium carbonate. Partly crosslinked grades include NP1021 (calcium carbonate) and NP1121 (PVC), both 79 Mooney. Nitriflex also supplies 39 percent ACN grades—NP 2130 (57 Mooney) and NP2150 (88 Mooney)—both with 12 percent calcium carbonate; the former is for injection molding, and the latter for adhesives. Twenty-eight percent ACN grades for improved low-temperature flexibility, such as NP2170 (57 Mooney, 12 percent calcium carbonate), are also available.

Internal mixers can usually accommodate rubber bales (generally 25 kg), as well as powder or crumb forms. Useful grades include Krynac® 33.30, 33.45, 33.55, 33.70, and 33.110. The *xx.yy* designation here means a target ACN level of *xx* and a median Mooney viscosity of *yy*. With Nipol® grades, *xx.y* is sometimes used instead. Useful grades for blending with PVC include Nipol® 35–8, 35–5, and

33–3, and also DN 36.50, 36.35, and 33.50. Crosslinked grades in bale form include Krynac® XL 3410. NBR bales can be obtained with strippable film packaging, as well as wrapped in film that will melt in normal internal mixer cycles. The Paracril® bale grades developed by Uniroyal are now supplied by ParaTec Elastomers, and the Goodyear Chemigum® grades by Nitriflex (Harwick Standard).

15.2.2 Mixing NBR/PVC Blends

NBR powders have a strong affinity for plasticizers. If they are added before plasticizer addition, this can lead to agglomeration and a heterogeneous dry blend. In a commonly used dry blend procedure, NBR powder is added after all other ingredients have been incorporated and the batch cooled to 40–60 °C, or in a second step, when cooling is not available. If the shear input is sufficient to disperse the NBR powder rapidly (30–60 s), it may be added during the cooling step. The cooled dry blend may be processed directly by extrusion or injection molding, or fluxed and palletized with suitable extrusion equipment. In cases where a dry blend is fed to an internal mixer for fluxing, NBR may be added in this step. In extruder fluxing, considerable shear is needed in the feed and first heat zones. These are usually set at 140–150 °C, with the remainder of the barrel at 160 °C, and the head and die at 170 °C. A *L*/*D* ratio of at least 20/1 should be used.

In preparing NBR/PVC blends in an internal mixer, with powdered NBR, all ingredients may be loaded in a single step, with mixer temperatures set high enough to provide rapid fluxing. When using NBR in bale form, this is usually added first, with stabilizers and often part of the filler content, followed by the remaining ingredients. Use of preblended NBR/PVC enables a variety of internal mixing techniques, including high-speed "upside-down" loading cycles with mixers of modern rotor design.

15.2.3 Processing NBR/PVC Blends

Extrusion The NBR grades typically used in blends tend to have considerable side-chain branching. This contributes to improved surface smoothness and dimensional stability. The improved hot melt stability enables extrusion of complex profiles and thin walls. When partially crosslinked grades of NBR are used, there is a reduction in die swell and shrinkage, often permitting higher line speeds. NBR/PVC blends are particularly suitable for wire and cable applications. When used in cable jacketing, the NBR content inhibits migration of plasticizer into the insulation during service or accelerated aging, thus maintaining the electrical properties of the latter. (Although NBR is not a particularly good insulator, its electrical properties are far better than those of ester plasticizers.) There is similar improvement in volatile loss of plasticizer.

Calendering Partially crosslinked grades of NBR are usually used. A minor fraction improves surface smoothness and reduces edge feathering, enabling higher line speeds. Embossed surface retention is improved, as well as the improvements in resistance to extraction and volatile loss noted above.

Injection Molding The most significant processing parameter in injection molding is compound melt viscosity. Usually non-crosslinked, low- to medium-Mooney-viscosity grades of NBR are used.

15.2.4 Properties of NBR/PVC Blends

Consider a base compound containing, for example, 80 parts DOP per 100 of PVC (80 phr), versus addition of 30 phr of a low-Mooney-viscosity non-crosslinked NBR and removal of 10 percent of the DOP content (8 phr). This is a common ratio to maintain approximately the same Shore A hardness—here in the range of 60–65. Melt viscosity will be found to be somewhat higher after replacing 8 phr DOP with 30 phr of a low-Mooney-viscosity NBR, for example with Krynac® 33.30. The increase is likely to improve extrusion and calendering, but is not so great as to prejudice injection molding. Similarly, die swell will be greater, and may require adjustment to extrusion parameters. Tensile strength, hardness, and abrasion resistance will be largely unaffected, but flex resistance will be dramatically improved.

In the same example, if a partially crosslinked, medium-Mooney-viscosity NBR is used instead (e.g., Nipol® 1411), melt viscosity will be considerably higher, but die swell will be cut dramatically. The resultant compound will have higher tensile strength and greatly improved abrasion and flex resistance. The compression set of both variations will be lower than the control. The major benefits to NBR levels higher than 30 phr are in abrasion and flex resistance. At ratios of 50/50 and 70/30 NBR/PVC, the product is best treated as an elastomer. Such blends are routinely mixed in Banbury® or similar mixers (generally for extrusion applications such as hose covers and cable jackets), and are vulcanized by the action of sulfur/accelerator systems or via peroxide or radiation crosslinking.

Plasticizer retention is essential to performance throughout the service life of flexible PVC. The most commonly used plasticizers are monomeric esters, which lend good end-use performance, ease of processing, and low cost. Plasticizer loss can arise through volatilization, extraction or migration into adjacent media. Replacement of 5–8 phr of common phthalate plasticizers with 30 phr of 33 percent ACN NBR will provide very noticeable improvement in retention of ultimate elongation after 70 or 168 hours at 113 °C heat aging, provided that a suitable antioxidant is included to protect the blend. Further improvement results from substitution of 50 phr NBR for 10–15 phr low-molecular-weight ester plasticizer. Heat aging is also substantially improved in tests run for 70 hours at 135 °C. The greatest improvements are found with the use of partly crosslinked NBR grades.

Similar improvements are gained in room temperature extraction resistance to aliphatic solvents (e.g., hexane), vegetable oils, and ASTM Type II fuel (60 percent isooctane, 40 percent toluene). Retention of elongation is also improved after exposure to ASTM #3 oil for 7 days at 100 °C. Of course, better results are obtained using combinations of NBR and polymeric plasticizers in PVC. Such compounds are typically only slightly changed after 70 hours' 135 °C heat aging or 7 days at 100 °C in ASTM #3 oil.

The use of 30 phr of 33 percent ACN NBR greatly reduces plasticizer migration into, or chemical stresscracking of, polystyrene, acrylics, ABS, or rigid PVC. Levels below 20 phr do not have a useful effect. Typically, 30 phr is used, replacing 5–10 phr monomeric plasticizer.

Although superior to Neoprene and Hypalon®, NBR/PVC blends do not have as great resistance to UV light as pure PVC. Thus, nonblack compounds should be protected with titanium dioxide and UV light absorbers. The latter have been commonly chosen from the benzotriazole class. New hindered amine stabilizers have been introduced (e.g., NOR HALS 833® from Ciba), that are resistant to hydrogen chloride. These should be considered for NBR/PVC compounds (except if tin mercaptide stabilizers are used). All NBR/PVC compounds should contain antioxidants of broad compatibility (e.g., Irganox® 1076).

15.2.5 NBR/PVC Applications

Compounds to compete with olefinic TPEs are typically based on blends using 50 phr of a 33–35 percent ACN crosslinked medium-Mooney-viscosity NBR, plus a polymeric plasticizer, ESO, stabilizer, phosphite costabilizer, and antioxidant. These have excellent heat aging, oil, and fuel resistance. Use instead of 30 phr will lead to similar properties, but a more thermoplastic, less elastomeric composition. Compounds for injection molding are also typically in the range of 30 phr NBR; however, in this case they are not crosslinked, but have a low Mooney viscosity plus a monomeric plasticizer. Compounds for foamed applications use 30–40 phr of low- to medium-Mooney-viscosity NBR, often crosslinked, monomeric plasticizers, foam structure control agents, and typically 0.5–2.0 phr azodicarbonamide, generally with an activator or activating stabilizer.

Wire and cable jackets may use as much as 100 phr NBR, often a blend of crosslinked and non-crosslinked grades (generally 33–35 percent ACN, 35–60 Mooney viscosity). Dibasic lead phosphite is being replaced in such compounds with calcium/zinc stabilizers. Such compounds will have modest plasticizer levels, and are best considered semirigid for formulating purposes; that is, they may benefit from lubricating processing aids such as Acryloid® K-120 N.

NBR is also used to modify PVC/ABS blends, particularly for automotive crash pads. A typical triblend may be based on 75 phr of ABS resin and 25 phr of a medium-Mooney-viscosity, usually crosslinked, NBR, plus a polymeric plasticizer, filler, pigments, antioxidant and stabilizer. The dibasic lead phosphite originally used in such blends is being replaced with calcium/zinc stabilizers plus phosphite costabilizers.

Interesting compositions are obtained by blending a pre-crosslinked NBR with either a solution PVC terpolymer with pendant —COOH groups (e.g., Ucar® VMCH) or a suspension-polymerized equivalent. Such blends can then be compounded much like synthetic rubber, and vulcanized by the crosslinking action of metal oxides or salts. The products have resistance to heat distortion comparable to vulcanized elastomers.

15.3 PVC/EVA BLENDS

EVA compatibility with PVC increases with VA content up to about 65–70 percent VA, and then declines. EVA copolymers with less than 40 percent VA have limited compatibility and use. In the range of 8–28 percent VA, they are used as flatting agents in flexible PVC to provide a matte finish, usually as concentrates in PVC, at levels of 3–5 phr. Useful grades include Elvax® 150 and 250 (DuPont), with 32 and 28 percent VA, respectively and Ultrathene® UE662 (Equistar), with 18 percent VA. Above 40 percent VA, useful compatible blends result. In the range of 45 percent VA, such blends are useful as impact modifiers in rigid PVC for exterior applications. A typical example is Baymod® L 2450 (Lanxess, formerly Bayer), which is available as a cryogenically ground powder for use in dry blends, partitioned with 7 percent PVC. An alternate is Baymod® L 2453, partitioned with 7 percent PVC plus 3 percent silica, the latter facilitating incorporation.

In flexible compounds, high-VA EVA serves as a highly permanent plasticizer, comparable, and sometimes used with, polymeric plasticizers, and leading to high resistance to migration, extraction, and chemical resistance. In comparison with NBR, little in the way of elastomeric character is gained, but heat resistance, low-temperature brittleness, and weatherability are superior. Generally, the coefficient of surface friction and oil resistance are lower. As with NBR, an antioxidant system must be provided. General purpose antioxidants, such as Irganox® 1010, are used in combination with phosphites, such as Irgafos® 168. Thus, the phosphite content of the blend is usually a combination of one active in PVC and another synergistic in EVA.

EVA is almost always used in combination with a monomeric plasticizer. Such compounds find use as protective films adhered to substrates by the action of surface tension. A useful mixing procedure is to add the EVA after the monomeric is absorbed at the "dry point." This avoids softening the EVA and interfering with its incorporation. In flexible PVC compounding, EVA is often used in pellet form rather than powder (Levapren® 450 being the pelletized equivalent of Baymod® 450). When properly mixed, PVC/EVA blends tend to process more easily than corresponding NBR blends. EVA in the 40–45 percent VA range is also available from Japan Polyolefins under the trade name J-Rex® and from Hyundai Industries under the trade name Seetec® EVA.

There has been occasional use of high-VA copolymers (60–75 percent VA) in PVC as permanent plasticizers in soft flexible compounds. The Levapren® pellet line includes grades ranging from 40 to 80 percent VA, the first two digits indicating the VA level. There is, in addition, a granular product for dry blending, Baymod® L 2418, with 68 percent VA.

EVA–carbon monoxide (EVA–CO) terpolymers (Elvaloy®, DuPont) also form blends with PVC that are useful in footwear, roofing, and liner applications, and in medical devices. Generally, 2–3 phr replaces one of monomeric plasticizer for equivalent hardness. The most commonly used grade is Elvaloy® 741. Typically, 35–70 phr are employed. These blends are more elastomeric in character than with pure EVA, and provide similar high resistance to extraction and migration. Low-temperature flexibility, aging, and weathering are better than with NBR. Blends are mixed similarly to PVC/EVA, except that temperatures in processing must not exceed 400 °F (204 °C), to prevent decomposition. The latter is acid-catalyzed. With blends containing VA, liberation of traces of acetic acid often occurs. This may not be adequately scavenged with general purpose PVC heat stabilizers. The latter can be reinforced in such blends with several phr of fine-particle magnesium oxide or (in critical or clear articles), with trace levels of polycarbodiimide (Stabaxol® P, Lanxess).

Alternating ethylene–carbon monoxide copolymers are not very compatible with PVC; otherwise their high heat distortion temperatures would suggest their use as heat distortion improvers. Nevertheless, reinvestigation might be considered. Various grades are available from SRI International under the trade name Carilon®. The product was developed by Shell Chemical, and the technology was given to SRI (formerly Stanford Research Institute).

PVC/EVA is also produced by grafting techniques through vinyl chloride monomer (VCM) polymerization either in solution or suspension in the presence of EVA polymer. Such products are described in Chapter 3. Such interpolymers find use in special purpose cable jackets, medical devices, and protective footwear. Another potential use is as a compatibilizing agent for otherwise incompatible PVC/LDPE blends.

15.4 PVC/CPE BLENDS

Aside from its use in rigid PVC as an impact and processing modifier, there is an interest in the use of chlorinated polyethylene (CPE) in pond liners and roofing. These are based on semicrystalline grades of CPE; the compound may be vulcanized or thermoplastic in use. PVC is added as a reinforcing polymer. Such blends are customarily mixed in a Banbury® or similar internal mixer. Typically, CPE polymers with 42 percent chlorine are used, such as Tyrin® 4211P (Dow). A similar grade, Weipren® 4042 (Yaxing Chemical) is distributed widely, as are grades from Daiso of Japan, under the trade name Daisolac®.

Similarly, thermoplastic grades of chlorosulfonated polyethylene (CSM), such as Hypalon® 45 (DuPont), are sometimes reinforced with PVC in roofing and pond liners. Such blends are also most conveniently mixed in an internal mixer. Often, such blends are formulated to crosslink in service by the reaction of metal oxides with CSM aided by atmospheric moisture. Blends of both CSM and CPE with PVC have also been used in such applications.

Although all of the blends described in this section are outside of the mainstream of PVC compounding, knowledge about their use may suggest innovations to the formulator.

15.5 PVC/ABS BLENDS

ABS is either a blend or a graft polymer of styrene/acrylonitrile (SAN) plastic with polybutadiene (PB) rubber. The latter ranges from 30–35 percent by weight ABS, in grades used for blending with PVC for calendered, injection-molded, and extruded applications, to 60–70 percent in grades for use as an impact modifier. In the former category, PVC contributes rigidity, strength, and flame retardancy, as well as low cost, while ABS provides flexibility, impact resistance, and toughness. As compared with conventionally plasticized PVC, PVC/ABS provides improved heat distortion characteristics, plus excellent resistance to chemicals, migration, and extraction. An important use is in calendered or extruded sheet for deep draw vacuum forming to produce luggage shells and automotive crash pads. The latter application requires a low-fogging grade, such as Blendex® 102S (32 percent PB, Chemtura). Other sources include the Novodur® P2 series (Lanxess) and the Terluran® GP grades (BASF).

PVC/ABS has also been used for weather-resistant profile capstocks. A useful grade is Blendex® 131 (35 percent PB), which is also suitable for footware, film, and sheet. Dark-colored capstock often uses acrylate–styrene–acrylonitrile (ASA) blends with PVC. Somewhat better heat distortion characteristics are typical. A common grade is Amsan® 587 (Chemtura), which is also available as a ground powder (587s). Another is Geloy® 1226 (GE Polymerland).

PVC/ABS and PVC/ASA blends are widely available from custom compounders and polymer suppliers, including Novatec, A. Schulman, Solvay, ComAlloy, Shuman, PolyOne, Denka, AlphaGary, Georgia Gulf, and Spartech. This is particularly useful if they must contain conductive carbon black, for example, to aid electrodeposition of metallic coatings. An example is Royalite® R63 (Spartech).

15.6 PVC/POLYURETHANE BLENDS

Thermoplastic polyurethanes (TPUs) are block copolymers of reinforcing, hard isocyanate segments alternating with soft polyester or polyether segments. Their major characteristics include elastomeric character, high strength, and outstanding abrasion resistance. PVC/TPU blends usually use polyester-based urethanes. These are more compatible and tend to have better flow, but have relatively poor water resistance. Before mixing blends with PVC (or processing in general), TPUs are typically dried for 2 hours at 100–105 °C at low relative humidity. Generally, TPU polymers in the range of 70–80 Shore A hardness are used. Prevalent grades include Estane® 58213 and 58224 (Noveon), Pellethane® 2102-75A (Dow), and Desmopan® 5377A (Lanxess—grades also referred to as Texina®). Polyether TPUs have much greater water resistance than polyester grades, but lower oil resistance (although they are still comparable with PVC). A relatively high flow grade that might be considered is Pellethane® 2363-80A. Since NBR is compatible with PVC and TPU, it should be considered as a third polymer if mixing proves difficult.

Blends of PVC and TPU are typically plasticized to some extent with monomeric esters. Hydrocarbons such as paraffin wax should be limited to very low levels, because of incompatibility with TPU; ester or amide lubricants should be used instead. Active hydrogen (stearic acid, alcohols) should not be present, because of isocyanate reactivity. Low levels of Stabaxol® P are advisable with PVC/VA to scavenge acetic acid. With PVC homopolymer, efficient heat stabilizers are adequate. Active hydrolysis catalysts such as antimony oxide and organotin carboxylates will adversely affect the water resistance of polyester TPU blends.

Many users prefer to purchase PVC/TPU blends. Elastamax® HTE 2101 (PolyOne) is suggested as a V-0 grade for interior profile extrusion, and Geon® XV3811B as a general purpose grade for extrusion and molding. A range of grades is available from AlphaGary under the trade name Vynite®, and from Performance Plastics as Apilon®. Major uses include footwear, tubing, and flexible pipe. PVC/TPU interpolymers can also be prepared by VCM polymerization in the presence of dissolved or dispersed TPU. Such grades are available under the trade name Aron® (Gosei Chemical).

Blends with TPU are usually high (50–100 phr) in the latter, usually limiting flow characteristics. If, instead, PVC is blended with thermoplastic copolyester (Hytrel®, DuPont), levels as low as 5–30 phr result in notably improved abrasion and heat distortion resistance, and greater low-temperature flexibility. In the Hytrel series, long-carbon-chain soft ester segments alternate with short-carbon-chain hard ester segments, instead of hard isocyanate segments as in TPU. One might think that this would enable lower price structure, but, as yet, it has not.

15.7 BLEND SELECTION

The paramount criterion in using another polymer in PVC is cost-effectiveness. There are two general situations. In the first, the polymer in question is relatively low-cost, has good PVC compatibility, can be processed without undue difficulty, and lends a balance of properties hard to reach with PVC itself. In such cases (NBR, CPE, EVA, and EVA-CO), there is considerable industry background, a number of applications, and a history of formulation. A second category comprises polymers that add specific advantages to PVC (ABS and TPU) and become cost-effective in a more limited range of applications. It should be noted that most of the above blends are more elastomeric than PVC. In most cases, the blend serves as a thermoplastic elastomer. For that matter, flexible PVC could also be considered a TPE. The properties of the rubber/plastic interface are of interest for all nonstructural PVC applications and to the formulator.

CHAPTER 16

Flame Retardants and Smoke Suppressants

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16.1 INTRODUCTION

In the absence of flammable ingredients such as combustible plasticizers, PVC, with a limiting oxygen index (LOI) of about 37, does not ignite in air under ordinary circumstances. There are incendiary conditions under which unplasticized PVC articles would be destroyed, but these are considered to be beyond the scope of amelioration via formulating. Rigid PVC articles have, from the point of view of the formulator, been thought to be nonflammable. This has come into question with the development of vinyl wood fiber composites containing significant fractions of finely divided oak, maple, or pine, as sawdust or pulped cellulose. At loadings of 40–70 percent wood fiber, ignition temperatures over 400 °C are found, per material safety data sheets of suppliers, as well as ratings of V0 per UL94 and self-extinguishing per ASTM D 635 (see Section 17.7).

In Western Europe, studies have begun on increasing the LOI of rigid vinyl construction components to the range of 45–50 or more by the inclusion of

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flame-retardant (FR) additives. In North America, however, the area of formulating vinyl for flame resistance remains that of flexible and semirigid compounds. Addition, for example, of 60–100 parts per 100 of resin (phr) of an ester plasticizer will lower the oxygen index to 20–22, which is low enough to fail most flame resistance tests (Section 18.8). Even 10–20 phr of an ester plasticizer will lower the oxygen index to the range of 25–30, which is typically adequate to pass horizontal but not vertical flame tests.

The use of plasticizers that are themselves flame retardants is discussed in Chapter 9, as well as formulating so as to optimize their effect and to minimize their tendency to be less efficient than flammable plasticizers. Chapter 9 also considers combustion mechanisms. A useful review of the latter has been given by Green.[1] This chapter presents the use of inorganic additives as flame retardants and smoke suppressants as a basis for formulation for specific applications. These additives can be divided into antimony compounds and derivatives; the class of metal hydroxides, carbonates, and basic carbonates; and a further range of molybdenum, zinc, and iron compounds.

16.2 ANTIMONY COMPOUNDS

Antimony compounds are the most commonly used flame retardants for PVC and other halogenated polymers, mainly because of their efficiency in reducing flame spread at relatively low levels, often 2–7 phr, without adverse effect on physical properties or heat stability. In hydrocarbon polymers, such as EPDM, containing halogenated flame retardants, antimony trioxide is commonly used at a 10–15 phr level. There is no evidence that antimony trioxide causes any loss of electrical properties, such as increasing dielectric constant, in either hydrocarbon or halogenated polymers. It is thought to react with halogen sources at flame temperatures, forming volatile antimony trichloride (boiling point 283 °C) or related volatile products, which disrupt chain reaction oxidation of C—H bonds in the gas phase.

Antimony trioxide (CAS 1309-64-4) has oral LD_{50} values in rodents of 3–3.5 g/kg, in the category of "slightly toxic" hazardous substances (in comparison, aspirin is 5–10 times more toxic). The World Health Organization (WHO) has mandated a level of less than 20 μg/l antimony in drinking water (common levels found in spring water are of the order of 1 μg/l). Nevertheless, PET articles are under attack in Europe because of water extraction of 0.4–1.1 μg/l antimony trioxide polymerization catalyst. The basis of this agitation is suspicion of carcinogenicity resulting from published reports of chromosome damage in laboratory rodents fed substantial amounts of antimony trioxide.[2] In feeding studies with levels corresponding to likely industrial exposure, Newton et al. concluded that antimony trioxide is not carcinogenic.[3] It remains listed, however, on nearly all regulatory documents as a possible carcinogen, despite the efforts of the International Antimony Oxide Industrial Association (IAOIA). Up-to-date developments may be found at their site: www.iaoia.org. Antimony trichloride (CAS 10025-91-9) is, at room temperature, a corrosive solid poison, with an oral LD_{50} in rats of 525 mg/kg.

A conclusion that the vinyl formulator should consider is that it is likely to become expedient to replace antimony-based additives with alternatives. This is particularly unwelcome to the wire and cable formulator already faced with demands to eliminate the use of lead-based heat stabilizers, and who has found that their replacement with calcium/zinc systems has led to, among other problems, decreased flame resistance. Duplication of the primary antimony-based mechanism requires volatilization of an at least potentially multivalent, relatively nontoxic metal whose chloride or oxychloride is a Lewis acid. Candidates might include tin, titanium, zirconium, or bismuth. Interestingly, alkali metal and ammonium hexafluorotitanates, zirconates and stannates interfere with ignition of bimetallic (nonlead) battery electrolytes.[4] Although such additives are worthy of study, it seems rather unlikely that direct metal substitutes for antimony trioxide will be found that also offer relatively low cost. One approach is to formulate with phosphorus replacing antimony, using phosphate plasticizers (Chapter 9). Which approach is most promising is a function of the application.

Typical properties of FR grades of antimony trioxide include melting point 656 °C, specific gravity 5.5, and lead and arsenic levels below 0.3 percent. Although antimony trioxide is often written as Sb_2O_3, an Sb_4O_6 pyramid is a more accurate description of the solid phase. The grades sold are predominantly 1–2 μm cubic crystals, the low aspect ratio and structure lending behavior, in regard to mechanical properties, comparable to (very dense) calcium carbonate. It is not normally used to provide a high specific gravity, because of increased expense compared to barytes. Antimony trioxide (Mohs hardness 2.5–3) is less abrasive than calcium carbonate (Section 6.2) and has a higher refractive index (2.0–2.1), lending it value as a white pigment. Various gray shades can be formulated, particularly for cable jackets, without any need for titanium dioxide. The dielectric constant of antimony trioxide, 3.8–4.4, is, however, not sufficient for replacement of titanium dioxide (where dielectric constant is too high for precise measurement) as a UV light absorber (Section 4.5). Gray cable jackets can, however, be formulated for UV light resistance with combinations of antimony trioxide and low levels of N110 SAF or an equivalent carbon black.

The pigmenting effect of antimony trioxide may be considered adverse where bright or pastel colors are desired, because of the need to use higher levels of expensive colorants. Low-tinting grades of antimony trioxide having larger crystal size are therefore available—typically at a cost premium, and usually stating the tinting strength versus standard oxide as 100 percent. Such grades, rather than those described merely as "low-tint," should be used where color specifications must be met. Furthermore, flame retardant performance may be affected. It is generally advisable to formulate a robust compound and develop cost savings through use of the best possible processing equipment. Low-tint grades, for example, may be 2–3 μm (US Antimony), 2.0–2.5 and 2.7–3.3 μm (two grades from Campine), or 4–5 μm (Chemico). In many cases, these could not be used interchangeably.

Antimony trioxide of particle size finer than standard is also available, which increases pigmentation value (upto a point—a submicron colloidal grade would scatter some incident light, but not act as a pigment). Although used in engineering plastics and thought to improve FR characteristics, this does not appear to be the case with vinyl. Antimony trioxide is refined from domestic ore by US Antimony, which supplies a standard 1.1–1.8 μm grade (HT), a 2–3 μm low-tint grade (LT), and a polyester catalyst 0.4–0.8 μm grade (VF). Comparable types based on international sources of ore (mainly from China), are supplied by Arkema Group, Campine, Chemico, Chemtura, China Antimony, Nissan Chemical, Oriental Metal Chemicals, Penox, Produits Chimiques de Lucette, and Sica. In addition, there are others specializing in ultrapure grades for fiber manufacture and electronics. The circumstance that most antimony trioxide is imported into the United States has led to severe changes in price and occasional shortage. This has resulted in the appearance of extended grades; these are typically as effective as would be expected from the percent antimony trioxide content.

Dispersion of antimony trioxide in vinyl is usually not a problem except with plastisols mixed with low-shear equipment, in which case paste dispersions in plasticizer should be considered (available from Kenrich and Flow Polymers). Dispersions may also be considered in dry-blend mixing because of the dusty nature of the ingredient and regulatory requirements, for example, the OSHA Permissible Exposure Limit (PEL) of 0.5 mg Sb/m^3. For large-scale usage in dry blending or internal mixing, the most cost-effective procedure in the long run is to use antimony trioxide powder in returnable semibulk packages (or bulk delivery) with enclosed automated metering and delivery systems, as is widespread with addition of lead stabilizers. The capital expense is not trivial, but will eventually be recaptured in volume pricing. It is difficult to estimate the cost savings in decreased risk of OSHA citation, but it is certainly a factor. With such systems, the user must establish that antimony trioxide (or other ingredient) from different sources will behave suitably in handling and delivery. With bulk systems in general, safeguards against contamination and related quality problems must be intensified because of the extent of product that will be affected. Nevertheless, these are the steps in process improvement vital to the strength of the vinyl industry.

Several of the above suppliers offer grades wetted with plasticizer to reduce (but not eliminate) dusting, analogous to wetted grades of lead stabilizers, often at little or no added charge (e.g., under the trade name Thermoguard® by Chemtura). These are convenient with minor usage of antimony trioxide inconsistent with investment in contained systems. Before implementation, it should be determined that resultant levels of antimony in air meet regulatory standards for worker operation with dust mask protection. Pumpable paste dispersions are used with plastisols and in some dry blending operations; in some cases, they are mixed with plasticizer prior to injection. Such dispersions add cost, which may be recaptured in higher output from improved processing.

An alternative available with high-intensity mixing is to use preweighed antimony trioxide (or combination with lead stabilizer) in a sealed low melt EVA or PVC bag (adding the weight of the bag to the resin content). Suitable packages are supplied by Rhein Chemie (or, for lead–antimony combinations, Flow Polymers). This route should be considered as an intermediate step to bulk handling or an alternative if volume is not large.

A common form of dispersion used with antimony trioxide is that of small (1×3 mm) virtually dustless extruded strands, typically at an active level of 85–90 percent in a lubricant binder that promotes incorporation and may improve processing, possibly offsetting increased cost. This type of product is available from Chemtura; it should be considered in cases where less than major quantities are used in high intensive mixers. An alternate is to use pelletized concentrates, usually of about 80 percent activity in an EVA binder. An appropriate use is via a proportioning meter in pellet extrusion, particularly in cases where a standard base compound is sometimes adjusted with antimony trioxide for a specific application. Such products are available, for example, from Rhein Chemie.

The improvement in flame resistance of vinyl compounds with addition of antimony trioxide is a function of flammable plasticizer content. At levels of 50–60 phr of ester plasticizer, oxygen index can be brought into the 25–30 range with 4–9 phr. At levels of 80–100 phr, it is hard to exceed an oxygen index of 25. At high plasticizer levels, therefore, it is generally useful to replace part of the ester plasticizer with phosphate (Chapter 9). High levels of antimony trioxide (6–12 phr) are often associated with "afterglow,"—nonflaming combustion after the ignition source is removed. In addition, the gas-phase interference of antimony leads to incomplete combustion, with smoke formation, the smoke consisting of carbon particles. Thus, smoke suppressants, which also tend to decrease afterglow, are often combined with antimony trioxide in proprietary products. One that has had considerable use in vinyl is Thermoguard® CPA (Chemtura), an antimony–zinc–barium product, specific gravity 4.9. Others include Smokebloc AZ-11 (Sb–Zn–Mg) and AZ-12 (Sb–Zn–Mg–Si), also supplied by Chemtura. The cost-effectiveness of such combinations varies with the market price of antimony trioxide. It is often preferable to devise one's own combination of additives. In situations where facilities and time for product development are limited, it may, on the other hand, be preferable to make use of combinations developed by suppliers.

The process engineer should keep in mind that antimony trioxide is an excellent hydrolysis catalyst, the reverse feature of its being an esterification catalyst for polyesters. As a result, polyesters use sodium antimonate, not a hydrolysis catalyst, for FR applications. With plasticized vinyl containing antimony trioxide, care should be taken not to exceed standard processing temperatures. Evolution of parent alcohol from an ester plasticizer, often of distinct odor, is an indication that processing temperatures have become excessive.

Antimony pentoxide (CAS 1314-60-9), specific gravity 3.8–3.9, is considerably more expensive than the trioxide, contains 75 percent Sb rather than 83 percent, and, therefore, must be used at a higher level, typically 10 percent, to provide equivalent FR properties. It is, in addition, an oxidizing agent capable of accelerating degradation by, inter alia, consuming phosphite costabilizers, and must be formulated with care (as with perchlorate salts; see Chapter 4). Nevertheless, it finds use in clear plastisol, solution, and latex coatings because of its low pigmentation value. The typical product, having submicron particle size, is supplied by PQ under the trade name Nyacol®, and by Campine, Chemico, Lucette, Oriental Metal Chemicals, and US Antimony. Dispersions in water of 30–50 percent activity are supplied by

PQ and Chemico; these are useful in latex compounding (Section 3.1.4), and, because of the ease of obtaining good dispersion, are generally preferable even in filled or pigmented latex compounds.

Sodium antimonate, $NaSbO_3$ (CAS 15432-85-6), specific gravity 3.7–4.8, is also used where low tint is desired. It is listed in some parts of the world under another CAS (15593-75-6) and sometimes as $NaSb(OH)_6$ (33908-66-8). Sodium antimonate is used mainly to modify glass for high clarity, and for flame retardance in PET and PBT because of its low activity as a hydrolysis/esterification catalyst. It has been used in vinyl occasionally for low-tint applications, being of lower cost than antimony pentoxide. Grades are usually 1–5 μm. Since lead and arsenic content is higher than with antimony oxides, use in vinyl should be discouraged. That being said, it should be noted that toxicity is not high, with oral rodent LD_{50} values of greater than 5000 mg/kg. Chemtura supplies 2 and 5 μm grades: Pyrobloc® SAP-2 and -5. Other suppliers include Chemico, Hammond Group, Lucette, Oriental Metal Chemicals, Teck Cominco, and US Antimony.

16.3 ALUMINA TRIHYDRATE

Alumina trihydrate (ATH), also known as aluminum trihydrate and hydrated alumina, $Al_2O_3{\cdot}3H_2O$ (CAS 21645-51-2), specific gravity 2.42, Mohs hardness about 3, is effective in vinyl at high loadings (50–75 phr) particularly in combination with phosphate plasticizers. Flammable ester plasticizer content needs to be limited to 0–35 phr in order to succeed with routine flame tests. It is not an electrical-grade filler (with a dielectric constant of about 7), but is useful in jacket compounds. With a refractive index of 1.57, it has lower pigment value than calcium carbonate, but its acid-absorbing capability improves heat stability. ATH functions by consuming heat input in volatilization of bound water, cooling of the flame by the water released, which may also interfere with gas-phase chain-reaction oxidation. It also improves char formation, lowering transmission of incoming heat, and notably reduces smoke formation. ATH probably catalyzes the water gas reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad (1)$$

The effect is consumption of carbon particle smoke. Since the water gas reaction is thought to involve metal carbonyl intermediates, it is likely that traces of iron in ATH are involved. Iron compounds such as ferrocene are also effective, but add color and prejudice heat stability in vinyl. In a probably related application, ATH suppresses carbon tracking under high potential in electrical insulation.

In vinyl, ATH grades of about 1 μm average particle size are generally used, since FR effectiveness appears to improve with decreasing particle size. At high loadings, blends of 1 μm and slightly coarser grades are sometimes used. Process temperatures must be held below 200 °C to prevent premature ATH decomposition with resulting porosity. Thus, surface-treated grades are often used. These include stearate treatment to improve flow, and silane treatment, for example with aminosilanes, to improve mechanical properties as well as flow (Section 6.7). The user may find it more economical to treat ATH during mixing. One alternative is to treat ATH with 0.7 percent of a titanate coupling agent (LICA® 38, Kenrich), which promotes char formation. ATH and other hydrous fillers are routinely used with processing conditions (e.g., wire extrusion) that permit escape of minor amounts of gases such as water vapor. Care should be taken in using hydrous ingredients with processes that are less tolerant, such as injection molding.

Commercially available grades of ATH recommended for vinyl include Hymod® M1500 SL, stearate-treated, and 9402, silane-treated, from Huber; Hydral® 710, untreated, and silane-treated Lubral® alternative, from Almatis; Superfine SFE-4 and -7, from Alcan; and Martinal® OL 107 LE, from Albemarle. These grades are either precipitated, yielding directly a fine particle size, as with Hydral, Martinal, and Alcan Superfine, or ground to equivalent size, as with Hymod. The various grades should not be presumed interchangeable without testing. Comparable grades are also supplied by PAG (Polymer Additives Group).

The costabilizer hydrous Type A zeolite (CAS 1318-02-1), an aluminosilicate (Chapter 4), is also a flame retardant of the same general function as ATH and adds to FR properties, particularly with lead-replacement mixed metal stabilizers. There are typically no problems with premature decomposition during processing when used at low levels as a stabilizer, but such could be the case if it were used at filler loadings (decomposition temperature 240 °C). A 3–6 μm grade, Advera® 401, is available from PQ.

16.4 MAGNESIUM COMPOUNDS

Magnesium hydroxide (MH), $Mg(OH)_2$ (CAS 1309-42-8), specific gravity 2.36, 2.5 Mohs hardness, refractive index 1.57, decomposes at 325–350 °C and may, therefore, be processed safely in vinyl compounds under otherwise reasonable conditions. It functions in an analogous manner as ATH, generates a higher yield of water, but is somewhat more expensive. It is also less inert than ATH, with a measurable oral rodent LD_{50} of 8500 mg/kg. Reactivity also manifests itself in color hold, where pinking may be observed with uncoated grades. As with ATH, both stearate and silane treatments, particularly aminosilane, are available. Grades recommended for vinyl are typically 1–2 μm in average particle diameter. These include Versamag® UF (Rohm & Haas); Kisuma® 5A (Kyowa); Magnifin® H7C, stearate-coated, and H7IV, aminosilane-coated (Albemarle); Vertex® 100 and Zerogen® 50 SP, silane-treated (Huber); and MagShield® UF (Martin Marietta), available with 1, 2, and 3 percent stearate coating. With stearate coating, the goals are improved color hold and processability; with silane coating, there are improvements to mechanical properties as well. For special purpose applications, food-grade products are available. Grades for use in vinyl are also available from Polymer Additives Group.

Basic magnesium carbonate (BMC), also referred to as hydromagnesite and magnesium hydroxycarbonate, has been described as $4MgCO_3{\cdot}Mg(OH)_2$ with either four or five molecules of water of hydration, specific gravity 2.16, and decomposition at about 250 °C (assigned CAS 7760-50-1, but sometimes as a variant of magnesium carbonate, CAS 546-93-0). Its use in FR plastics has been discussed by Rigolo and Woodhams.[5] The conclusions are that surface treatment of hydrous fillers is important in FR performance and that the effects of combinations of such fillers are additive and not synergistic. This indicates that hydrous filler–polymer interaction to form thermally nonconductive char is an important factor in performance, as well as volatilization of water of hydration. BMC is also an effective secondary stabilizer when used in replacement of calcium carbonate. Usually, 1 μm grades are used in vinyl. These are available as Carbomag® TL (Solvay) and Elastocarb® BMC (Rohm & Haas). BMC as well as magnesium hydroxide should be considered in formulating to minimize corrosive gas emission during combustion (Section 18.8).

A related product consists of a fine-particle (0.5 μm) blend of BMC with calcium magnesium carbonate (huntite), $Mg_3Ca(CO_3)_4$, Ultracarb® UF (Minelco), specific gravity 2.5, with a 300 °C decomposition temperature. The fine particle size leads to modest reinforcement as compared with standard grades of calcium carbonate and to excellent hydrogen chloride absorption not only on combustion but during degradation generally. Advantages in overall balance of properties through use of blends of hydrous fillers of different particle size and morphology would be anticipated but, are as yet, unreported.

Hydrotalcite, magnesium aluminum hydroxycarbonate (CAS 12304-59-9), commonly described as $Mg_6Al_2(OH)_{16}CO_3$ plus water of hydration, but somewhat subject to variation, is often used as a hydrogen chloride absorber in lead-replacement stabilizers and as a costabilizer with organotins (Section 4.4.1.1). Some grades have a decomposition temperature high enough (230 °C) to warrant consideration as an FR hydrous filler, although one of substantial cost. These include Kisuma (Kyowa) Alcamizer® MHT-PD and Sued Chemie Sorbacid®, both in the range of 0.5–1.0 μm, low Mohs hardness of about 2, and low-tint, with a refractive index of about 1.5.

16.5 ZINC COMPOUNDS

The most widely used zinc compound for FR applications in vinyl is zinc borate, (ZB): either $4ZnO{\cdot}6B_2O_3{\cdot}7H_2O$, a low-tint fine powder (CAS 1332-07-6), sold as ZB-467 (Chemtura) and by Polymer Additives Group, or $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ (CAS 12536-65-1), a high-tint fine powder, sold as ZB-223 and as Firebrake® ZB (Rio Tinto, formerly Luzenac), FireChoke® ZB (Royce), and Charmax ZB400 (Polymer Additives Group). It should be noted that none of these products contain waters of hydration, but are rather cyclic O—B—O trimers with B—OH groups. The "467" zinc borate decomposes at 280 °C and the "233" at about 300 °C, both suitable for vinyl. Both ZB-467 and 233 are in the 3–5 μm range. Both are nontoxic to mammals (oral rodent $LD_{50} > 10$ g/kg), but, as with zinc-containing compounds generally, toxic to fungi and bacteria, lending biocidal properties, and raising the possibility of ecotoxicity. The Firebrake® ZB products are available in Fine (2–3 μm) and XF (1–2 μm) grades, as well as standard ZB (5–7 μm). In addition, there is a Firebrake® 415 grade with much zinc content, $4ZnO \cdot B_2O_3 \cdot H_2O$, and higher density (specific gravity 3.7) that decomposes at 415 °C, and is suitable for engineering plastics.

The zinc borates promote char formation and intumescence in the solid phase, suppressing afterglow and smoke formation by development of a glassy inorganic coating. In addition, there is gas-phase interference with combustion, most likely by chlorine-containing boron compounds. As a result, the combination of antimony trioxide and zinc borate in vinyl is excellent for providing low-smoke FR characteristics—with one caution. Zinc borate is a ready source of zinc for formation of zinc chloride and rapid degradation to char, useful in combating combustion, but not in routine processing. In consequence, high stabilizer levels are needed. Calcium and lead borates show very little FR activity in vinyl; it is the combination with zinc that is effective.

Similar effects are shown by zinc hydroxystannate (ZHS), $ZnSnO_3 \cdot 3H_2O$ (CAS 12027-96-2), and zinc stannate (ZS, ZST), $ZnSnO_3$ (CAS 12036-37-2). ZHS requires close processing control, decomposing slightly over 180 °C; ZS is stable to 300 °C. Both are char formers and provide flame reaction interference, presumably through Sn—Cl species. ZHS in addition supplies water of hydration and is the more popular in vinyl formulating. ZHS has a specific gravity of 3.4, is low-tint with a refractive index of 1.9, and is typically supplied in 1–3 μm particle size as Flamtard® H (Alcan Chemical) and Charmax® LS-ZHS (Polymer Additives), and also by Niknam of India. ZS has a specific gravity of 5.5, is also low-tint, and is supplied in 1–3 μm particle size as Flamtard® S and Charmax® LS-ZST, also by Parchem. A combination ZHS/ZB product is available as Flamtard® B1.

An interesting variation has been to coat lower-cost FR fillers such as ATH and MH with ZHS. Such products are supplied by Petroferm as ZHS/ATH and ZHS/MH at 20–50 phr levels, replacing 20–50 phr of ATH or MH plus 2–5 phr of ZHS, typical use levels. ZHS-coated fillers, including calcium carbonate, have been studied extensively by Hornsby and co-workers.[6] Studies of the filler interface indicate that the char-forming mechanism is completely a function of the particle surface, thus making coated fillers useful.[7] One would expect the gas-phase effect of Sn—Cl to diminish, however, with tin content as it does with antimony.

A magnesium/zinc combination product is available from Chemtura as Ongard® 2, specific gravity 4.4, 1.5 μm particle size, designed primarily to aid char formation in rigid and semirigid vinyl. A further combination with AOM is also available as Smokebloc® AZ-40.

16.6 MOLYBDENUM COMPOUNDS

Only one molybdenum compound has found significant use in vinyl, ammonium octamolybdate (AOM), $(NH_4)_4Mo_8O_{26}$ (CAS 124411-64-2), specific gravity 3.18, sold as average 4 μm grades, Smokebloc® AOM-100 (Chemtura) and AOM-WA

(Climax), and 1–2 μm grades, AOM-A2 and Charmax® AOM (Polymer Additives), as well as by H.C. Starck GmbH. Decomposition is at 250 °C. It is an effective char former and probably the most effective gas-phase smoke suppressant for vinyl; it is used commonly in combination with zinc borate to lower overall cost. AOM is likely effective in eliminating smoke carbon particles by Reaction (1) above through molybdenum carbonyl intermediates. As with ZB, AOM is hardly a vinyl stabilizer. Reaction with hydrogen chloride at processing temperatures can lead to formation of an intense chromophore of variable composition, "molybdenum bronze." Stabilization levels, therefore, are typically very high compared with non-FR compounds. Shen and co-workers have reported that combinations of AOM and ZB are additive in FR properties, not synergistic.[8] This suggests that at least one, probably ZB, is not active in the gas phase.

A number of other molybdenum compounds are used in paint and coatings. These include molybdenum trioxide (Climax), as well as zinc and calcium/zinc molybdates, sold under the trade name Kemgard® (Sherwin Williams). Although effective as intumescent flame retardants and smoke suppressants in coatings, as yet they have not proven so in flexible vinyl compounds. This may relate to the fuel source in flexible vinyl being mainly mobile plasticizer rather than flammable polymer; these additives might be revisited, if need be, in unplasticized compounds. With low levels of flammable plasticizer, it is possible to replace about half the antimony oxide content with molybdenum trioxide with similar LOI results.

The potentially lowest-cost inorganic additives for smoke suppression would be based on iron, except that if they are active enough to provide iron carbonyl intermediates in a flame, they are likely to be vinyl prodegradants generally, and possibly toxic. An excellent example is ferrocene, dicyclopentadienyl iron (CAS 102-54-5), a reddish solid that has remained a laboratory chemical despite strong smoke suppression in many matrices. Reasons for this include its toxicity (rodent LD_{50} values in the range of 200–800 mg/kg) and ability to promote polymer degradation in a wide variety of service conditions. A derivative that might be investigated, bis(diphenylphosphono)ferrocene, Binap® is available from Rhodia. Carty and co-workers have investigated a reaction product of ferrocene with chlorendic anhydride that also might be of interest.[9] The gas-phase interference by metal carbonyl intermediates may also be available by formulating with metal acetyl acetonates. FR improvements in vinyl with Fe, Co, Ni, and other derivatives were noted by Tian and co-workers.[10] The use of calcium and zinc acetylacetonates (β-ketoesters) as stabilizers is very old, dating to work of Darby.[11] Combinations of alkaline earth and metal carbonyl-forming ketoesters as FR stabilizers may well be worth further investigation.

Many intumescent flame retardants are based on mixtures of polyols, amines such as melamine, and phosphates such as ammonium polyphosphate. These have not been much used in vinyl because of potentially degradative effects and because of equivalent protection being supplied by phosphate plasticizers. Ammonium polyphosphate (APP), used mostly as fertilizer, is available in polymer grades from Clariant under the trade name Exolit® AP. Similarly, there seems to have been little use of red phosphorus, available as Exolit® RP. Work in other areas suggests investigation of these unusual additives, perhaps coated with silicones, which can also be char forming and smoke suppressing. This technology has been reviewed by Pape.[12]

16.7 FLAMMABILITY TESTING

Section 18.8 discusses ASTM D 2863 LOI testing as well as procedures of UL94 (ASTM D 3801), D 635 horizontal testing, D 1354 cone calorimeter procedures, the E 906 heat release test, E 84 Steiner tunnel large-scale tests, E 662 NBS smoke testing, and the D 5485 corrosive gas and E 1678 toxic gas tests. These are the procedures most prevalent in the United States. There are literally scores of similar tests and also many of a special purpose nature, required by individual regulatory bodies. There is considerable effort under way to rationalize and correlate test procedures throughout the world.

Most rigid vinyl articles will pass the tests listed above without addition of flame retardants. For example, pressure pipe as formulated with standard lubricant, polymeric modifier, and stabilizer systems (Section 4.2.3) will have an LOI of 48–50 and pass Steiner tunnel and NBS smoke tests. It would not, however, conform to some European standards in past use and to EU specifications under development. For such applications, the combination of 1–3 phr flame retardant with 1–3 phr smoke suppressant would be needed. The exact level depends on the type and level of polymeric modifiers in use, CPE being, for example, more useful in flame tests than nonhalogenated modifiers. The latter, on the other hand, will tend not to contribute to smoke density. In rigid vinyl, it is likely that FR/LS standards can be met with systems not containing antimony.

In vinyl plasticized with various levels of a readily flammable ester, for example DOP, LOI will rise gradually with each part of antimony trioxide, up to about 5–7 parts, at which point it will tend to level off. At about 75 phr flammable plasticizer, this will limit compositions to about 25 percent LOI, usually sufficient to pass horizontal but not vertical flame tests. At 30–50 phr plasticizer, 5–7 phr antimony trioxide will provide an LOI of 30–35, adequate for simple vertical tests. Substitution of zinc borate for antimony trioxide in such systems will result uniformly in lower LOI, but use instead of a 1:1 blend will generally duplicate results with antimony trioxide alone because of their synergistic effect. Zinc borate does not appear to interfere with gas-phase action of antimony plus chlorine. One-third replacement of flammable plasticizer with chlorinated paraffin will result in a greater increase in LOI per part antimony trioxide added. The effects of replacement with FR phosphate plasticizers are discussed in Chapter 9.

At significant levels of flammable plasticizer, highly FR vinyl compositions require not only additives such as antimony trioxide, zinc borate, or proprietary combinations, but also replacement of calcium carbonate or calcined clay with an FR filler such as ATH or BMC. Results in flame tests are generally enhanced by coating the FR filler to improve dispersion and surface contact with the vinyl matrix and by fine particle size. These factors favor development of char with poor thermal conductivity, and probably promote release of water of hydration to the flame.

16.8 SMOKE SUPPRESSION

Vinyl compounds tend to burn with a smoky flame, with NBS smoke obscuration values that can be as high as over 300 D_{mc} in the nonflaming and over 600 in the flaming mode (Section 18.8). These are notably higher than found in combustion of aliphatic hydrocarbons and their polymers, and relate to the formation and combustion of aromatic structures. As the level of hydrogen available for combustion drops, flame temperature decreases and the formation of carbon particle smoke increases. Dilution with calcium or other carbonates that react with hydrogen chloride generally lowers smoke density by 25–35 percent in both modes. Use instead of hydrated fillers has a greater effect, 40–50 phr of ATH or MH typically reducing smoke emission by half. Use of antimony trioxide almost invariably increases smoke density, the effect leveling off with loading at about the same point as that of diminished FR effect, and increasing with loading of plasticizer.

Smoke formation is strongly reduced by char-forming additives that coat the fuel with a noncombustible glassy layer and by synergists that promote flame oxidation of carbon smoke particles (Reaction 1). The additives having the widest usage in vinyl—AOM, ZB, and ZHS—appear to do both. Applications requiring reasonable flame resistance (LOI of about 30) and smoke suppression (LS), such as building and appliance wire, can be formulated by replacement of the customary 2–3 phr of antimony trioxide with 3–4 phr of a 50 percent blend with ZB, or by replacing filler with a ZHS-coated product, or by partial plasticizer replacement with phosphate, plus an SS additive. Results of such combinations are given in Tables 9.3, 9.7, and 9.8. Starting-point formulations for common applications are given in Tables 9.9, 9.10, and 9.11. Resin selection for FR applications is presented in Section 2.6.1.4 and current stabilization systems in Section 4.4.1.1. In addition, suppliers of FR/LS additives mentioned in the foregoing are dependable sources of recommendations. A listing of suppliers and useful review of combinations in use has been developed by Kroushl.[13]

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CHAPTER 17

Vinyl Wood Fiber Composites

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17.1 INTRODUCTION

Vinyl wood fiber composites are now common in decking, railings, moldings, picture frames, and other profile extrusions. Such products are sold by, among others, Andersen Window, Certain Teed, Compos-A-Tron, Crane Plastics, Lida Plastics of Japan, Marley Mouldings, Profile Solutions, Royal, Tri-Ex Composites, and Youngstown Plastics. Most of the expansion in this rapidly growing area has come about in the last two decades. It is worthwhile to consider how this has happened.

Wood fiber in the form of sawdust, generally referred to as wood flour, has been a compounding ingredient for many decades in natural and synthetic rubber products, where, when properly bonded to the polymer matrix, it provides reinforcement and wear resistance. Thus use was found in semihard rubber floor casters, solid forklift tires, and the like. Bonding to elastomers is typically achieved by inclusion of phenolic resins. In the 1970s, Monsanto commercialized a treated cellulose fiber derived from wood pulp, under the tradename Santoweb®, as a result of the work of Coran and co-workers.[1] Some success was found as a reinforcing agent for articles subject to anisotropic service loads, such as vulcanized rubber hose components. Special head

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and die configurations were developed at Monsanto, then a supplier of extruders, for extrusion of cellulose fiber-reinforced hose.[2] In 1983, Goettler reported an extension of this work to plasticized vinyl.[3] Bonding to the resin was achieved with isocyanates. A typical formulation used up to 50 parts per 100 of resin (phr) cellulose fiber with 55 phr butyl benzyl phthalate plasticizer, about 2 phr bonding agent (Akzo Nobel Vulkabond® would be suitable), and 6–10 phr stabilizer and colorants. Omission of bonding agent markedly lowered tensile strength and modulus. The compounds were suggested for vinyl hose—in principle to replace hose tube plus reinforced hose cover with a single reinforced extrusion. Clearly, this might also be extended to vinyl belt constructions. Presumably, the cost of Santoweb® fiber has militated against this use. With recent developments in wood fiber technology, there is reason to revisit these applications. The most significant conclusion for the formulator from this early work is that useful vinyl wood fiber composites require the use of bonding or coupling agents to adhere the hydrophilic fiber to the hydrophobic polymer.

Cellulose fibers from wood pulp having aspect ratios of 15, 35, and 45/1 with residual moisture levels below 7.5 percent are available from CreaFill Fibers under the trade name CreaTech™. They report improved flexural strength and impact resistance as compared with 40-mesh oak fiber.

17.2 DEVELOPMENT OF BONDING AGENTS

Significant developments were reported in 1990 by Kokta, Maldas and co-workers at the University of Quebec[4] using dried hardwood (aspen) sawdust and cotton cellulose fiber in plasticized vinyl compounds. As might be expected, the best overall balance of properties resulted from use of the polymeric isocyanate polymethylenephenyl isocyanate (PMPI), followed by diisocyanates TDI and HMDI, with the least effect from a monomeric isocyanate. Use of isocyanates as adhesion promoters is discussed in Section 12.7.

Critical levels of bonding agent were found, above which properties declined. Uniform distribution of bonding agent was found to be critical, leading to use of predispersions in DOP plasticizer. Substantial increases in modulus were found, at the expense of elongation and impact strength. In the following paper, the authors extended the work to softwood (spruce) and emphasized the importance of homogeneous distribution in mixing.[5] During the 1990s, work had begun on urethane wood fiber composites, for example by Wolcott and co-workers.[6] It would be interesting to consider addition of a polyol and development of PVC–urethane wood fiber composites, leading to products with improved abrasion resistance. This would be analogous to composites made with ground tire scrap for high-impact flooring, for example by Dodge Regupol. Actually, ground rubber scrap might be considered as a minor ingredient with wood fiber because of the biocidal effect of vulcanization residues. When added to wood mulch, 10–20 percent ground tire scrap suppresses growth of spore-shooting artillery fungus, a suburban nuisance.[7] Ground rubber scrap has been investigated as filler for PVC; levels up to 20 percent ground footware scrap yielded useful properties in tin mercaptide-stabilized compositions.[8]

At about the same time, the University of Quebec group reported on the use of silane coupling agents in plasticized vinyl wood fiber composites.[9] Vinyl, acrylyl, epoxy, and aminosilanes were used to alter the wood fiber surface, with γ-aminopropyl triethoxy silane, A-1100 (GE), yielding the best results, presumably from amine displacement of labile chloride and bond formation to the polymer. Aminosilanes are broad-spectrum adhesion promoters for vinyl through use of this mechanism (Section 12.7). Mercaptosilanes would be expected to yield similar results. What was not tried in these experiments was reaction of aminosilane (or mercaptosilane) with the resin prior to addition of wood fiber previously coated with, for example, vinyl triethoxysilane, plus hydrolysis catalyst such as dibutyltin dilaurate, as in standard silane crosslinking (Section 3.3.4). Such an approach would be worth consideration. Commercially available silane coupling agents for PVC are discussed in Section 6.7.

The surface energy and chemistry of the wood fiber vinyl interface was the subject of a 1998 report using surface tension measurements and spectroscopic techniques.[10] It became clear that thorough drying and impurity removal from the wood fiber was vital to successful reaction with bonding and coupling agents, and, further, that merely matching the surface energy of the fiber to that of the polymer matrix was insufficient for development of adhesion strong enough to provide a good balance of properties. Surface tension of solid surfaces was calculated from contact angles formed by a fluid of known surface tension (glycerol). The contact angles were determined from contact diameter viewed from above using the Axisymmetric Drop Shape Analysis method[11] to maximize precision ($\pm 1^\circ$). X-ray photoelectron spectroscopy (XPS) was used to determine the chemistry of changes to surfaces that led to altered surface tension. This clearly showed bonding of the coupling agent to the wood fiber surface. But merely altering the surface energy to match that of the polymer did not provide strong adhesion to PVC, as shown by the strength of corresponding lap shear joints, as it is known to with polyolefins.[12]

The aminosilane A-1100 was found to provide excellent bonding to suitably treated wood fiber—much superior in this regard to dichloroethylsilane, phthalic anhydride, or maleated polypropylene, although all of these led to a wood fiber surface similar in surface tension to PVC. It seems likely that silanol condensation with surface hydroxyl groups on the wood fiber is combined with amine displacement of allylic chloride from the resin. Aminosilanes remain the coupling agents of choice, with considerable formulating latitude, since mono-, di-, and polyaminosilane species are available. Use of mercaptosilanes should also be considered, particularly in compositions stabilized by organotin mercaptides.

In an interesting paper of 2004, Jiang and Kamdem reported that both flexural strength and unnotched (but not notched) impact strength of vinyl containing 40 percent red oak fiber were improved by fiber treatment with copper–ethanolamine complexes.[13] This was attributed to increased fiber-to-matrix adhesion. It was not reported whether such complexes deteriorated aging and weathering properties, but in at least one of the three compounds tested, stabilization used an extreme level of organotin, 3 percent Mark® 98 (Chemtura).

This was followed by the finding that the naturally occurring polymer chitin and its derivative, chitosan, could be used as coupling agents.[14] Chitin is an analog of cellulose with one acetylamino group replacing a (the same) hydroxyl group in the hexose structure. It is a primary component of crustacean shells, of low cost, and available (TCI America). Chitosan is deacetylated chitin, thus having one hydroxyl of each hexose ring in cellulose replaced by an amine group. Such products might be anticipated to be similar in action to aminoamide adhesion promoters (Section 12.7). They might, in fact, be considered potential low-cost replacements. The following compounds were investigated:

PVC ($K = 66$)	100
Wood fiber	75
Plastistab® 2808 organotin	2
Calcium stearate	1.5
Paraffin wax	2
Paraloid K-120	2
Paraloid K-175	2
Paraloid K-334	10
Chitin	0–7.5
Chitosan	0–7.5

Ingredients were added to a high-intensity mixer, then twin-screw extruded and molded into test panels. Optimum levels for best flexural strength and modulus were 6.67 percent chitin and 0.5 percent chitosan. DMTA measurements indicated major gains both in storage and loss moduli at temperatures from 30 to 70 °C, without significant change to the glass transition temperature as measured by the tan Δ peak maximum.

The high levels of processing aids in vinyl wood fiber composites should be noted. A study of properties versus level has been reported.[15] The test compound was as follows:

PVC ($K = 58$)	100
Emulsion PVC ($K = 74$)	4
Barium–lead stabilizer	2.6
Calcium stearate	0.6 and 2.4
Calcium carbonate	12
Wood fiber	50
External lubricant	0.3
Processing aid	0–12

The processing aids comprised Paraloid® K-120 and K-130, and Kaneka PA-20. In general, the best balance of properties was obtained with 6–12 phr of processing aid. (Calcium stearate at 2.4 phr appears excessive; anomalous losses in mechanical properties were reported.)

A number of proprietary surface treatments for wood fiber for vinyl composites have emerged. These include Glycolube® WP-2000 (Lonza), TPW-012 and 251 (Struktol), described as lubricants, and Mark® W15 (Chemtura), described as a stabilizer/lubricant. Combination colorants and surface treatments are available from Accel, Clariant and Techmer PM.

17.3 VINYL FOAM WOOD FIBER COMPOSITES

The natural area in which vinyl wood fiber composites could compete is in wood replacement, vinyl providing a more or less impervious barrier to rot and decay without the effort needed to coat and refinish wood. The composites are, however, too dense and too expensive. The realization that this could be overcome by expanding vinyl wood fiber composites probably occurred to a number of technologists in the 1990s. By the middle of that decade, expanded vinyl wood fiber decking and window components were being sold. The rationale for expanded products was reported in 1997.[16] Microcellular foamed vinyl–wood fiber composites were produced by compounding resin (Geon 103 EPF76) with treated or untreated wood fiber (Interfibe Corp.) in a high-intensity Pfleiderer Gelimat® G-1 mixer, compression-molded into panels, saturated under 5.51 MPa pressure of CO_2 for two days, and then expanded by heating at ambient pressure in a glycerol bath, a technique previously described.[17] Experiments used DOP plasticizer at 13.5, 20, and 30 phr. Surface treatment was with A-1100 aminosilane. In treated samples, increasing DOP from 13.5 to either 20 or 30 phr enabled increased expansion and higher measured CO_2 content, but in untreated wood fiber composites, this did not occur despite comparable melt flow characteristics. With poor fiber-to-resin adhesion, escape of gas was instead favored. In treated samples, higher DOP levels had little effect. Foam density and cell size could be controlled within limits by variation of expansion temperature and time, but, in general, not as closely as with unfilled foamed vinyl. The lower density of wood, however, partly compensated for lower overall expansion.

Although foaming led to lower overall tensile strength (MPa) of a vinyl-treated wood fiber composite, specific tensile strength (MPa cm^3/g) was independent of void fraction.[18] Foaming led to a general loss of tensile modulus and corresponding increase in ultimate elongation, the result being a notable improvement in notched Izod impact strength versus the unfoamed composite, as long as an effective wood fiber surface treatment was in place. Without proper treatment, little or no improvement in impact strength was found.

At about the same time that Dey and co-workers reported expansion of rigid vinyl by extrusion injection (Section 14.1) of argon or CO_2,[19] Park and co-workers at the University of Toronto developed single-screw vented extruder and twin-screw tandem extruder processes for continuous CO_2 injection into polyolefin wood fiber composites.[20] The method has much to recommend it; the absence of chemical blowing agent and the need to control its decomposition precisely are clear advantages. The possibility of unwanted interaction of chemical blowing agent with other ingredients would be eliminated, as would the need for activators. The process should be considered for high-output products such as decking boards. Suitable equipment could be obtained from, for example, Kawata Mfg of Osaka. There have, however, been no reports to date of commercial processes using extruder gas injection into vinyl wood fiber composites, suggesting that engineering problems have been encountered.

In 2000, Patterson reported properties of extruded expanded rigid vinyl composites with 40 percent 80-mesh hardwood fiber (American Wood Fibers), dried to 0.5–1.0 percent moisture; surface treatment was unstated.[21] Samples containing either sodium bicarbonate or azodicarbonamide at unspecified levels were extruded and expanded to two densities, 0.60 and 1.01 g/cm^3, based on an unexpanded density of 1.31 g/cm^3. At the lower density, the product was comparable in mechanical properties to pressure-treated pine, with anticipated improved durability and eventual cost advantage with rising lumber prices. Formulations of this type appearing in commercial literature are typically as follows:

PVC ($K = 65$)	100
Wood fiber	50–80
Processing aid	2–6
Lubricating processing aid	0–1
Calcium stearate	0.6–1.2
165 wax	1–1.2
Oxidized PE wax	0–0.2
Stabilizer	1–2
Azodicarbonamide, or	0.3–0.6
Sodium bicarbonate	1.5–2.0

A low level (0.2–0.3 phr) of biocide might be included; dichloro-octyl-isothiazolone has been reported to have excellent UV light resistance.[22] It is supplied by, among others, Rohm & Haas (Vinyzene® SB27). Predispersed blends of chemical blowing agents are available from Bergen (Foamasol®) and Clariant (Hydrocerol® PLC).

17.4 EFFECTS OF MODIFIERS

Solid vinyl wood fiber composites suffer from reduced impact strength, militating against the advantages of reduced cost, improved appearance and stiffness.[16,18] The effects of acrylic (Paraloid® KM-334, Rohm & Haas), CPE (Tyrin® 3615, Dow), and MBS (Paraloid® BTA-730L) impact modifiers were evaluated in the following compound:[23]

PVC (K=57)	100
Hardwood maple, 20 mesh	50

Plastistab® 2808 tin stabilizer	2
Calcium stearate	1.2
Paraffin wax	1
Paraloid® K-120	1.2
Paraloid® K-175	1
Impact modifier	0, 5, 10, 15, 20

Compounds were mixed in a high-intensity mixer (Papenmeier Type TGAHK20) to feed a Brabender 30/1 single-screw extruder running at 50 rpm at a 165–175–185–185 °C profile. The extrudate was compression-molded to form tensile (ASTM D638) and impact (D256) testing specimens. Addition of impact modifier led to decreased tensile strength and modulus in all cases, but had little effect on ultimate elongation. All three types of impact modifier led to improved Izod impact at −20, 0 and 20 °C, but the crosslinked acrylic and MBS types proved superior to 36 percent chlorine CPE. This behavior has been observed in other systems, and has generally been attributed to the greater ability of the crosslinked modifier to maintain a network morphology leading to crack dissipation despite a wide range of processing conditions.[24]

Subsequently, the use of CPE as an additive for vinyl wood fiber composites has been addressed by Dow Chemical and the effect of chlorine level studied.[25] Higher extrusion output rates with improved melt strength and elongation with 25 percent chlorine content CPE, Tyrin® 2500P, were reported, leading to reduced melt fracture and edge tearing.

When the above hardwood maple compound (except for the use of 30 phr wood fiber) was modified by sorption of CO_2 in static experiments, all impact modifiers increased loss of gas to the atmosphere.[26] This was less evident with crosslinked acrylic impact modifiers than with thermoplastic CPE. In practice, commercial compounds based on sodium bicarbonate or azodicarbonamide tend to use little or no impact modifier. They are, for example, not found in compositions described by Cope (Marley Mouldings) in a 1996 patent filing describing extrudable profiles.[27] No surface treatment was described for the wood fiber used in the following compound, but it cannot be concluded that none was in use:

PVC	100
Wood fiber	15–60
Calcium carbonate	4
Calcium stearate	1
Loxiol® 1875 ester lubricant	1.5
AC 629A PE	0.1
Mark® 1924 organotin	2
Azodicarbonamide	0.2–0.7
Kaneka K12 processing aid	7

There is similarly no mention of pretreatment other than drying to specified moisture levels in the 1998 patent filing by Finley (Andersen) directed to window components.[28] The compositions are stated to be those previously described:[29]

PVC (e.g., Geon 427)	100
Wood fiber	60–120
Titanium dioxide	15
Calcium stearate	1.5
EBS lubricant	2
Methyltin stabilizer	2
Acrylic processing aid + 5% regrind	7.5

In their process, an extruder is fed three inputs, the above (used in solid components) in pellet form, a blowing agent/surface treatment concentrate (Reedy Safoam® AP-40), and a foam stabilizer, Paraloid® K-415, in the ratio of 565/13.5/36.1. A profile of 175–175–185–185 °C barrel and 185 °C die led to melt temperatures about 199 °C.

The effects of foam modifying additives and residual water content formed the basis of a subsequent study based on the following:[30]

PVC ($K = 57$)	100
Hardwood fiber, 100-mesh	50
Plastistab® 2808 organotin	2
Calcium stearate	1.2
Paraffin wax	1
Paraloid® K-120	1.2
Paraloid® K-175	1
Azodicarbonamide AC-FA	0–1
Paraloid® K-400 foam modifier 0	0–10

Available moisture content of the wood fiber was varied from zero to 12 percent and die temperature from 170 to 210 °C, leading to a four-factor central composite design. Densities of 0.41–0.98 g/cm^3 were obtained. It was concluded that there was no synergistic effect between chemical blowing agent and moisture content of the wood fiber. Usable foamed compositions could be produced solely with wood fiber moisture if adequate levels of foam modifier were used. Nevertheless, as residual moisture content was increased, less foam modifier was needed to reach a given density. Furthermore, as residual moisture content was increased, processing temperatures needed for useful density levels decreased. The ultimate conclusion was that, with proper formulation and control, use of chemical blowing agents might be eliminated—an attractive avenue for further process development.

The effects of DOP plasticizer in the antiplasticization range (0–15 phr) of PVC containing 45 phr ground newsprint fiber has been studied.[31] An antiplasticization effect was found, extending to 7.5 phr DOP, as compared with 3.75 phr with unfilled PVC (Geon 103EPF76) in regard to tensile properties. With notched Izod testing, however, impact resistance of fiber composites improved steadily with plasticizer content, with no decrease at low levels as with unfilled PVC. One may conclude that minor amounts of plasticizer can be added to vinyl wood fiber composites generally without deleterious effects if chosen so as not to interact with other additives, such as coupling agents. This may be useful to the formulator seeking to incorporate rapidly and homogeneously items such as colorants or blowing agents in the form of dispersions in plasticizer.

17.5 STABILIZATION OF VINYL WOOD FIBER COMPOSITES

Wood fiber contains organic acids; pH can run to as low as 5–6. As a result, levels of stabilizer tend to be high as compared with ordinary vinyl compounds. Use of various stabilizers has been studied by Bacaloglu and colleagues in 40 percent wood fiber composites.[32] Best color hold at 204 °C (static) was found with 3 phr of Mark® 2270F butyltin mercaptide–carboxylate, followed by 3 phr Mark® 2289 dibutyltin maleate. Less effective were TS1091 and TS1147 calcium/zinc stabilizers at 3 phr, followed by 1.5 phr levels of Mark® 1900 methyltin, Mark® 1993 reverse ester tin, and 1.5 phr of the calcium/zinc stabilizers. Increasing the level of Mark® 1900 to 2.5 phr would lower the activation energy of degradation to bring it in line with the best above. It appeared easier to achieve extrusions of good appearance at various shear rates with organotin stabilization, a finding well known in empirical usage.

Another factor involved in discoloration, in this case of objects in contact with wood fiber composites, is tannin stain. Tannins are complex phenolic compounds produced by trees as biocides; therefore, the level found in wood fiber is variable. Air oxidation leads to dark-colored quinine-containing products that are water-soluble and which stain textiles, paints and coatings. Tannins can be complexed by aluminum salts to prevent surface migration. Products are sold by Halox Div., Hammond Group, under the tradename Xtain™.[33]

The first report of wood fiber composites being subject to microbial attack dates to 1998.[34] In this case, the matrix was HDPE. At about the same time, a report issued describing microbial attack on polyethylene membranes.[35] It is likely that microbial metabolism was limited to additives in the film. There is, moreover, good evidence that, under ordinary conditions, PVC polymers are not metabolized by microbes.[36] Composites made from the following compound were placed in contact with moist soil inoculated with a variety of fungi:[37]

PVC ($K = 66$)	100
Organotin mercaptide	2

Calcium stearate	1.5
Paraffin wax	2
Paraloid® K-334 impact modifier	10
Paraloid® K-120 processing aid	2
Paraloid® K-175 lubricating processing aid	2
Wood flour	50, 75, 100

At all wood fiber levels, fungal growth and hyphae (rootlet) development were found on surfaces in contact with fungal inoculated soil. This reflects the fact that there are exposed fibers at the surface; that is, there is less than 100 percent encapsulation. Thus, unless they are topcoated, fungal discoloration of exterior vinyl wood fiber components is likely. Topcoating exterior components with ASA or acrylics is, in all regards, a good idea, although adding cost. Of the various biocides popular for use in PVC, good results have been found, as mentioned above, with dichloro-octyl-isothiazolone. Biocides for use in vinyl are discussed in Section 4.6. Recent products designed for vinyl wood fiber composites include Carboquat® (Lonza) and Irgaguard® F3000 (Ciba). Ciba has also announced a combination additive to combat fungal attack and tannin stain, EB-43-25. Zinc borate, used at 1–1.5 percent in HDPE composites, requires very high stabilizer levels to inhibit zinc burn (when used as a smoke suppressant in cable jackets), and is rarely used with organotin stabilizers.

In an interesting sidelight, Wolcott and co-workers found that white rot (*Trametes versicolor*) infestation of highly loaded HDPE wood fiber composites actually improved mechanical properties because of the increased compatibility lent by proliferating fungal hyphae, presumably attracted to additives, such as stearates, found in the resin.[38] To date, no such effects have been found with vinyl. There is also possibility of bioremediation in the field. Certain species of parasitic fungi (e.g., *Debaromyces*), prefer to ingest mold and inhibit growth of common nuisance molds and mildew.[39] This has also been observed with *Trichoderma* and the bacterium *Pseudomonas fluorescens*.[22] An observation bearing on bioremediation is that bacteria that can ingest petroleum oil (e.g., as a result of spills) are encouraged in oil metabolism by the availability as well of more easily digestible food, leading to flourishing growth.[40]

The UV light-resistance characteristics of vinyl wood fiber composites are quite interesting. These were studied in a Q-Panel apparatus using a severe cycle of 8 hours at 60 °C under UV-B illumination followed by 4 hours condensation at 50 °C.[41] After 400 and 2600 hours, surfaces were examined and compared with the original via contact angle measurements, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The last is particularly illuminating. Prior to irradiation, the surface of composites showed a higher degree of oxidation as compared with PVC, increasing with increasing wood fiber content, mostly, as might be expected, in the form of C—O groups (one oxygen bonded to carbon). After irradiation, although the level of C—O structures increases dramatically with pure PVC, with composites it remains roughly the same. The incidence of C═O carbonyl groups increases with irradiation in all cases, but, after 2600 hours, is lower with composites than with pure PVC. In addition, the mechanical properties of the composites, unlike those of pure PVC, were largely unaffected. This is attributed to stress transfer from the polymer matrix to the load-bearing wood fiber resulting from successful encapsulation. The combination of XPS and scanning electron microscopy (SEM) pictures is particularly useful with composites, not only for gaining an understanding of cause-and-effect relationships, but also often simply to characterize what has resulted (from formulation variation) in a commercially useful product. It will be interesting to see if further insights can be gained by study of composite surfaces by atomic force microscopy (AFM).

Discoloration, however, remains an issue with vinyl wood fiber composites for outdoor application. UV light absorbers for vinyl are discussed in Section 4.5. Hindered amine stabilizers resistant to hydrogen chloride are now available, but require more expensive organotin carboxylate, rather than mercaptide, stabilizers, since they interact with the latter. A useful alternative is to include the hindered amine stabilizer in an acrylic or ASA topcoat over the wood fiber composite.

The effect of including 10 phr rutile titanium dioxide in a composite based on 30 phr aminosilane-treated 20-mesh hardwood maple fiber has been reported.[42] Samples were subjected to 1200 hours' UV-A exposure at 45 °C with water spray for 18 minutes every 2 hours in a Q-Panel apparatus. Protection with titanium dioxide limited ΔE color change to 4.34, as compared with 16.57 for an unprotected control. This remains more severe than with pure PVC: $\Delta E = 1.57$ with 10 phr TiO_2. FTIR measurements indicated notable retarding of formation of polyene linkages during light exposure by rutile at this level.

Another factor that must be considered with vinyl wood fiber composites is the presence of residual moisture in the wood. Changes in moisture level are known to lead to degradation of interfacial properties in composites.[43] Effects of freeze–thaw cycling on vinyl composites containing 50, 75 and 100 phr of 40-mesh maple or pine wood fiber have been reported.[44] The standard ASTM D 6662 soak, freeze, and thaw cycle was used as well as freeze–thaw only to separate the effects of water incursion and freeze–thaw cycling. Several conclusions were evident. The mechanical strength of composites containing less than 100 phr wood fiber was not significantly affected by freeze–thaw cycles. At 100 phr wood fiber, decreased encapsulation by the matrix led to increased moisture uptake as well as a rougher appearance, as noted on SEM. Volume swell increased with increasing wood fiber content, but was small compared with wood. The water-only portion of the cycling process had the greatest impact on flexural properties; property loss is likely attributable to the moisture effects on matrix–wood fiber adhesion. Durability in outdoor exposure in products such as decking is a matter of concern. A recent report indicated increased loss of mechanical properties in rigid PVC in outdoor aging in the presence of elevated levels of ozone.[45] It is not known to what extent this may apply to wood fiber composites. With rigid vinyl capped by protective layers, Summers and Rabinovitch have reported superior performance in retention of impact resistance using a semirigid vinyl topcoat formulated for outdoor use.[46] On a positive note, complete resistance of composites up to 80 phr wood fiber to aggressive termite species (*Coptotermes* sp.) has been noted.[47]

17.6 TYPES OF FIBER

Investigations of variation in fiber began some years ago. Using polymeric isocyanate treatment, Maldas, Kokta, and Daneault reported the differences in mechanical properties between aspen, spruce, and birch, and between sawdust, cotton fiber, and fiber from paper pulp processing.[48] Typically, aspen and birch provided better properties than softwood spruce. At 30 percent loading, the highest modulus at 1 percent strain was found with two types of treated pulp, followed by cotton fiber, and then treated sawdust. The effects of isocyanate treatment were more dramatic with sawdust.

Rigid vinyl 10–30 percent glass fiber composites have been developed by PolyOne using proprietary technology, and are sold under the trade name Fiberloc®. Investigation of wood-plus-glass fiber PVC composites is a natural extension. Treated and untreated wood fiber and silane-treated borosilicate glass of 14 μm diameter, $L/D = 52–61$, at total levels of 15, 25 and 35 percent, were varied in all wood-to-glass proportions in a 1992 report.[49] No surprising synergy was noted. Wood fiber treated with bonding agents was again superior to untreated as regards mechanical properties. Increasing glass content led, in most cases, to improved impact strength, as would be expected. In some cases, it seems that additional coupling agents added may have interfered with the effectiveness of the silane coating on the glass surface.

This area was reinvestigated by Jiang and co-workers using red oak wood flour and two types of 14 μm-diameter glass fiber: type S, high-strength glass (65 percent SiO_2, 25 percent Al_2O_3, 10 percent MgO) of $L/D = 57$, and type L, an optical grade of high-strength glass used in retroreflective beads, of $L/D = 457$, with varying proportions of wood and glass and total loadings of 45–60 percent.[50] Minor additions of type L glass significantly improved the impact strength of vinyl wood fiber composites without loss of flexural strength. No such effect was found with type S (both are rather more expensive than E-type borosilicate glass routinely used in plastics composites). This was attributed to the structure formed by high-L/D type L glass fiber. Wood particle and glass fiber to matrix were the most common failure modes. There is again the possibility of interfering surface effects. It would be of interest to revisit these experiments by blending premixed vinyl wood fiber and vinyl glass fiber dry blends (and fluxed compounds), and also through investigation of order of addition in single-pass mixes, particularly with general purpose grades of glass fiber. A range of the latter with different surface coatings for inclusion in various polymers is available from Lanxess (e.g., CS7917, with a polyamino sizing). It would also be of interest to investigate improvements to impact strength with combinations of glass fiber and impact modifiers.

Use of various grades of mica as a filler for vinyl is discussed in Section 6.3.3. As compared with calcium carbonate, greater flexural strength and dimensional stability, as well as lower thermal expansion and surface energy, are to be expected. At least one silane-treated grade is commercially available. Combinations of 200-mesh mica and hardwood fiber at overall levels of 15, 25, and 30 percent in vinyl have been reported.[51] As the wood fiber treatment was made increasingly effective, replacement with mica progressively deteriorated physical properties, both stiffness and impact resistance. There was little to choose between untreated wood fiber and mica. Again, it would be interesting to have this area revisited using silane-treated mica, with and without separate additions of the (hopefully) reinforcing agents. It would perhaps be more interesting to explore combinations with silane-treated wollastonite because of the greater improvements likely in impact resistance (Section 6.3.5).

17.7 MEASUREMENT OF COMPOSITE PROPERTIES

One of the most commonly used methods of examining the surfaces of composites is known as electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS). In this technique, a surface is contacted with low energy (1–2 keV) X-rays, which eject electrons from atoms of the sample surface. The energy content of the electrons is analyzed by a spectrophotometer to identify the emitting element and its environment, such as carbon bonded to carbon or hydrogen versus —C—O—, —C=O, and —CO_2 bonds. The incident X-rays must be monochromatic and of accurately known energy. Light elements are used, since line widths are proportional to atomic number. Typical sources include Al (K-α $E = 1.487\,\text{keV}$) and Mg (K-α $E = 1.254\,\text{keV}$). Although the X-rays penetrate deep into the sample, only electrons on the surface are able to escape, thus making XPS a surface analysis technique. Suitable equipment is supplied by, among others, Thermo Electron Corp. Those offering the analytical service include the Institute of Materials Research & Engineering (IMRE, Singapore, www.imre.a-star.edu.sg). The use of XPS in examining vinyl cellulose fiber composites has been employed to establish the esterification of cellulose surfaces by coupling agents such as phthalic anhydride and PP-maleic anhydride.[52]

A related technique is Auger emission spectroscopy (AES). Here, the surface is bombarded by a beam of electrons of known energy (20 eV–2 keV). The bombardment ejects an electron, whose collision with neighbors emits a photon, which finally causes ejection of yet another electron, referred to as an Auger electron. Usually K- and L-shell electrons are involved. The technique is very useful with heavy elements, and could be used to identify Pb, As, Ba, among others, on composite surfaces (as it is now used with semiconductor surfaces). AES can penetrate to no more than 50 Å (5 nm). Suitable equipment is supplied by, among others, JEOL.

In scanning electron microscopy (SEM), an electron beam (primary electrons) is directed to a specimen surface by beam condensers (analogous to lenses with a light beam) in a scanning mode, sweeping a grid, dwelling on points for a period of time determined by the scan speed, usually in the microsecond range. Interactions with the surface producing, for example, secondary electrons and backscattered primary electrons are detected by electrodes, illuminating pixels on a cathode ray tube (CRT) in proportion to the number of interactions at a specific site. The pattern of secondary electrons is used to provide topographical images of the surface. Backscattered primary electrons can provide the atomic number of the scattering atom. At one time, nonconductive surfaces were metallized prior to SEM analysis in vacuum; a more recent development is ESEM (environmental SEM) in which secondary electrons collide with gas molecules, the collisions amplifying the signal, eliminating the need for metallic coating. Suitable equipment is supplied by JEOL, Hitachi, and others. SEM has been used extensively to characterize wood fiber composites, effects of surface treatment and relation to expansion with gas.[53]

Surface chemical analysis can be built into SEM, with inclusion of equipment to provide energy dispersive X-ray analysis (EDX, sometimes also abbreviated as EDS or EDAX). X-rays generated by SEM electron bombardment of the sample surface are detected as a function of their energy (frequency), leading to the identity of the emitting atom. (When wavelength rather than frequency is analyzed, the method is referred to as wavelength dispersive X-ray analysis, WDX or WDS. Better resolution is obtained than with EDX, but at higher cost.) EDX or WDX would be useful for identifying metals present at composite surfaces.

Composite surfaces may also be examined by reflectance infrared spectroscopy (ATR = attenuated total reflectance, the intensity of absorption by the sample amplified by attenuating the control infrared beam mechanically). ATR spectra of solid surfaces are typically obtained using a Fourier transform infrared (FTIR) spectrometer. Such instruments differ from classical grating or prism infrared spectrometers in not recording spectral intensity directly as a function of wavelength (or frequency), but being based on an interferometer that permits the signal to be recorded as a function of the optical path difference between a fixed and a movable mirror. From the interferogram, intensity of the spectrum versus wavelength is calculated via a Fourier transform—hence the name. As compared with older methods, FTIR yields higher resolution and throughput in intensity. Suitable equipment is available from, among others, Nicolet and Perkin Elmer. The combination of FTIR and SEM has proven valuable in interpretation of composite behavior.[51] It is particularly useful when results of mechanical testing seem conflicting.

An extension of FTIR analysis directs a highly monochromatic beam at a very small area under view of an optical microscope—thus the reference to microscopic FTIR. Special detectors are used, often at liquid nitrogen temperature. The identity of small specks (such as found on extruder screen packs) can be determined. Areas of interest can be mapped microscopically to determine the distribution of ingredients. Uses in vinyl have been reviewed.[54,55] One that has been investigated is the receptivity of vinyl surfaces to printing and decoration.[56] Development of polyene sequences in vinyl wood fiber composites was followed, showing that polyene content increased with moisture level prior to processing.[57]

In order to separate plant pigments, Mikhail Tsvett invented chromatography in 1903. Liquid chromatography went unnoticed until rediscovered by Willstaetter, for which (in part) he received a Nobel Prize in 1915. Gas chromatography (GC) was invented by Fritz Prior in 1947, but was developed into a useful process by Martin and Synge, who shared a Nobel Prize in 1953. In GC analysis, a sample of a mixture is injected and swept, usually by helium, through either a capillary or a packed column, in either case coated with an active material to which it is anticipated that components of the mixture will interact differently, leading to different elution times, as with liquid chromatography. Samples must, therefore, consist of gases, liquids, or solids with appreciable vapor pressure under the conditions used. With inverse gas chromatography (IGC), this is reversed. The column packing is the solid or composite to be investigated, the retention times of neutral, acidic, basic, or otherwise reactive volatile probe compounds are determined. The technique was applied to cellulose and wood fiber by Dorris and Gray in 1979.[58] It has since been used to elucidate reactions of coupling agents with cellulosic fibers, showing that the effectiveness of aminosilanes relates to replacement of —OH on cellulose with —R—NH_2, with resultant affinity towards PVC.[59] A number of polymer wood fiber interfaces have been studied with IGC by Simonsen and co-workers.[60]

Processing characteristics are vital to the acceptance of all composite materials, but historically little had been reported since the early work of Goettler.[3] More recently, capillary rheometry has been used to calculate true viscosity and DMTA (Section 18.6) to determine storage and loss moduli of vinyl wood fiber (0–50 phr) composites at 40–75 °C, with and without 8 phr Paraloid® K-400 acrylic processing aid.[61] It was concluded that die swell is reduced by addition of wood fiber but increased with increasing level of processing aid at all levels of wood fiber reinforcement. Acrylic processing aid significantly increased the viscosity of unfilled PVC because of increased melt elasticity, but lowered the viscosity of the much stiffer composites.

Similarly, little work had been done on the effect of wood fiber on PVC fusion properties. In HDPE, processing conditions had been shown to be (not surprisingly) dependent on fiber mesh size and level.[62] The melting of a semicrystalline polyolefin is, however, much different from PVC grain fusion, the latter being the subject of an excellent review by Rabinovitch and Summers.[63] It was clear that fusion time and temperature were increased by the addition of wood fiber, as would be expected from its heat capacity, regardless of whether hardwood oak, maple, or ash, or softwood pine, was used.[64] Fusion time in a Brabender® roller blade mixing head (60 g) at 180 °C went from 46 s for unfilled (obviously rapid-fusing) compound to 130 s with 65 percent oak fiber, 164 s with ash, 244 s with soft pine and, anomalously, 480 ± 68.5 s with 65 percent hard maple. Fusion temperatures, 181 °C with unfilled, ranged from 198 to 201 °C with 65 percent wood fiber, regardless of type. Energy of fusion ranged from 6.6 kN m for unfilled or 22–35 kN m for pine, oak, and ash, but 54.3 ± 8.9 kN m for maple. All had been oven-dried for 48 hours at 105 °C to a moisture content of less than 1 percent. It is not clear whether species differences are chemical, morphological, or combinations of both.

In the above, the ash fiber samples derived from trees infested with the emerald ash borer. Processing appeared comparable to oak, a desirable composite species. Thus, it seems likely that diseased trees might be salvaged after removal for wood fiber composites as a supplementary source to timber and papermaking operations.

Statistical design of experiments is the subject of Chapter 19. Such experiments are used widely (but not as widely as they should be) in formulating vinyl. An example is in the comparison of treated azodicarbonamide (AZO) and sodium bicarbonate in the test compound:[65]

PVC ($K = 57$)	100
Tin stabilizer	2
Calcium stearate	1.2
Paraffin wax	1
Paraloid® K-120	1.2
Paraloid® K-175	1
Paraloid® K-400	5
100-mesh maple fiber	0 and 50
AZO or $NaHCO_3$	0.5

It was concluded that sodium bicarbonate and AZO (Sections 14.2 and 14.3) provided similar mechanical properties. Both, however, in unfilled PVC, yielded impact strength greatly inferior to microcellular foam produced by CO_2 absorption—providing, additional impetus to develop this method to commercial status.

Because of the relatively brief history of vinyl wood composites, a large number of references have been included in this chapter in the belief that further reading will assist the formulator.

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CHAPTER 18

Laboratory Methods

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18.1 INTRODUCTION

Vinyl compounds are prepared and tested for purposes including research, for developing improvements in processing and properties, for quality control validation, and for problem solving. Tests include conformance to specifications, and evaluation of processability and fitness for service. (The last is often not identical to conformance to published specifications.) Compounding and testing will typically require about 1 kg, a convenient quantity for preparation on a laboratory mill with rolls of 12 in (30.5 cm) width or with a Model B Banbury® internal mixer. Reconstruction of an existing compound can often be carried out with a 50–100 g sample using modern methods. In compound development, it is important to use known control samples, to use calibrated equipment, and to repeat tests routinely and when

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unexpected results are found. A finding that was unanticipated is commonly the basis for innovation.

ASTM D 1784 provides a number of categories for rigid PVC compounds based on type of resin, impact strength, tensile strength, modulus, deflection temperature, and chemical resistance. Flexible PVC compounds are categorized in ASTM D 2287 in terms of specific gravity, hardness, tensile strength, elongation, and low-temperature brittleness. Description of the compound in terms of its conformance to the above specifications is common, particularly when the details of formulation are proprietary. It is worth repeating that conformance to a given ASTM (or other) description does not ensure fitness for service in a specific application.

Vinyl formulating is a dynamic area of technology. The formulator should be aware that "standard" recipes found in textbooks of some years date are very likely to be obsolete and no longer competitive in the market. Similarly, all technologists realize that no laboratory method exactly duplicates factory conditions. With skill and experience, laboratory results nevertheless are predictive of full-scale behavior. In this sense, the formulator must also be a process engineer (or vice versa).

Vinyl formulators and testing laboratory managers should read ASTM Publication STP 1369, *Limitations of Test Methods*. It should not be anticipated that established test procedures will always yield unequivocal results. The occasional result that, based on past data, seems less probable is often the start of innovation.

18.2 PVC COMPOUND PREPARATION

High-Intensity Mixing The first step in compound preparation is most often to prepare a blend. Often this is done in the laboratory in a high-intensity mixer (such as manufactured by Henschel, Littleford, Papenmeier, and others), because this type of equipment enables mixing of a number of batches quickly and precisely, with rapid cleaning between batches. They are also easy to install and vent so as to conform to regulatory codes. These mixers operate on the principle of using rapidly rotating blades in a bed of particles in a compact container. The path of the particles is a spiral around the container axis, superimposed with gravitational force, creating a vortex movement similar to a fluidized bed. The container is usually jacketed for heating and cooling, either with cold water plus steam input or with circulating fluid from an external constant temperature device. (For laboratory use, the circulating oil heaters used with oil-heated torque rheometers are quite satisfactory.) The lid forms a tight seal, permitting evacuation of volatiles with a vacuum line, as well as injection of plasticizer while running.

Typically, resin is added first with the stabilization package, unless the latter is highly lubricating, in which case it may be added later in the cycle. With unplasticized compounds, often the resin, organotin stabilizer, calcium stearate fusion promoter, and impact and processing modifiers are mixed for 1–2 minutes before addition of fillers and pigments. In the absence of polymeric modifiers, the latter are added with the resin and stabilizer. When uniform dispersion has been reached, again usually in 1–2 minutes, external lubricants and lubricating processing aids are added. Lubricating Ca/Zn stabilizers may also be added at this point. Discharge is typically in the range of 90–110 °C. It should be noted that there are many variations in order of addition. Stabilizer may be added with the resin at ambient temperature or shortly thereafter at about 60 °C. Fillers and pigments of high abrasive index, such as titanium dioxide, are often withheld until the batch reaches 80–90 °C, to minimize equipment wear. In general, the greater the power input per weight of compound, the less critical the order of addition and the greater the output. If formulating for immediate factory use, duplication of existing production procedures should be the first step. It should nonetheless be appreciated that, on occasion, new compounds will arise that require modification to existing procedures, whether or not a given production department finds this inconvenient.

Low-Intensity Mixing If a rigid compound is to be processed as a dry blend, only high-intensity mixing is likely to be satisfactory (phonograph records are an exception). If the compound is fluxed and pelletized prior to further processing, low-intensity mixers can be used provided that fillers and pigments are easily dispersed (agglomerates broken up). The subsequent fluxing step generally does little to improve dispersion. Most rigid PVC applications require such substantial output that low-intensity mixers, which have about (or less than) half the output of high-intensity mixers of comparable capacity are impractical. Low-intensity mixers are supplied by Littleford, Ross, Sprout-Waldron, Toray, and others. A number of ribbon configurations are available, ranging from simple patterns useful for tractable compounds requiring little dispersive work and with rapid plasticizer uptake, to complex mixing and wall scraping arrangements to increase shear and promote incorporation. Before purchasing equipment, it is best to consult with the supplier as to the most useful ribbon blade configuration for the types of compound to be mixed.

Flexible PVC With plasticized compounds, the high-intensity mixer is preheated to about 100 °C. Resin and powder stabilizers are added. When the batch reaches 70–80 °C, plasticizer is metered in. It is often convenient to dissolve liquid stabilizer or other liquid ingredients in the plasticizer. At very high levels of plasticizer (100–130 parts per 100 of resin (phr)), it is common to add part of the plasticizer at 70–80 °C and the remainder when the batch reaches 85–90 °C. When plasticizer uptake nears completion, the batch swells and then appears to shrink (changes radically in appearance). At this point, fillers and pigments are added, preferably incorporating materials of low abrasive index first. In the range of 90–100 °C, the mixer speed is reduced and external lubricants added. With PVC copolymers and with rapidly solvating plasticizers, the above suggested temperature ranges would be notably lower. In some cases, the batch is completed by addition of a small quantity of solid material, producing a drier blend. If the compound is to be pelletized, this is a suitable opportunity for addition of talc to decrease pellet adhesion. Addition of functional filler or resin at this point as a drying agent should be considered only with low-end, high-volume products, because of the effect on uniformity of composition. The end of the batch is the correct point for addition of heat- or shear-sensitive ingredients, such as glass spheres, blowing agents, optical brighteners, and pearlescent pigments. In addition, ingredients intended for surface-active behavior such as release and antistatic agents can be added at the end of the batch or with external lubricants.

Cooling water is then circulated and the batch cooled while mixing to 35–40 °C. In some cases, with high-shear input, soft fillers such as calcium carbonate can be added with the resin, particularly with modest levels of plasticizer, improving output. This is infrequently done in the laboratory, other than to simulate a factory procedure. It should be avoided with submicron fillers such as precipitated calcium carbonate, since these often will absorb plasticizer more rapidly than the resin does, leading to intractable lumps. When using ultrafine fillers, lubricants as well as plasticizer should be incorporated first.

Using a ribbon blender, plasticized compounds are mixed in a similar manner. The mixer is preheated to 50–60 °C, charged with all solid ingredients except abrasive solids, and mixed, typically for 5–10 minutes, to 60–70 °C. At this point, plasticizer, preheated to 60–80 °C, is metered in (with spray heads in production, but often from a separatory funnel in the laboratory). The temperature to which the plasticizer is heated depends most often on the extent to which its viscosity requires reduction for easy delivery and rapid uptake. Old laboratory samples of plasticizer that may have oxidized should not be used. With proper stabilization, preheating temperatures as high as 105 °C have been used in production to maximize output that is limited by plasticizer uptake. Except to simulate production procedures, there is no need to do this in the laboratory (other than with plasticizers of extremely high viscosity). Overheating plasticizers whose absorption is very rapid (e.g., DOP) can lead to uptake more rapid than the distributive capability of a low-intensity mixer, leading to lump formation.

Liquid stabilizers and other small ingredients are often dissolved in the plasticizer for convenience. It should be noted that ribbon blenders without heating jackets are still found in some production facilities. In such cases, most of the heat input derives from preheated (sometimes overheated) plasticizer. Mixing with such equipment prejudices consistency and cannot be recommended.

Internal ester and amide lubricants are often added early in the batch, particularly with blends, to function as compatibilizing agents. Powder stabilizers can be added with the resin if they are nonlubricating; otherwise they should typically be added with external lubricants. Two-stage addition of plasticizer is again common with high loadings.

Whether plasticized or rigid, the contents (in the laboratory) are then spread on a stainless steel surface to cool further and to be examined visually for defects in dispersion. With plasticized compounds, this generally results in more uniform plasticizer absorption. It is likely that a period of standing improves rigid PVC compounds as well, subject to the caution that it may be unrepresentative of factory procedures.

If the goal is primarily process development, laboratory compound is best mixed in equipment similar to that mixed in production (the exception being if production plans conversion to high-speed intensive blending from more primitive methods). A ribbon blender jacketed for heating and cooling can be used in cycles similar to the above but typically longer. On the other hand, the capital investment in mixing equipment is much lower. This must be balanced against the increased laboratory space typically required by the low-intensity mixer's larger footprint.

Wet Blending In the absence of more sophisticated equipment, plasticized compounds can be prepared in the laboratory in an unheated planetary mixer, such as supplied by Hobart and used routinely in baking and other food preparation. Typically, liquid ingredients are dissolved in the plasticizer. All solids other than external lubricants are charged to the mixing bowl and mixed for 1–2 minutes, at which point the plasticizer is slowly added and allowed to be absorbed at ambient temperature, followed by any external lubricant. With modest levels of plasticizer, particularly with preheating, dry blends are obtained. In other cases, a damp blend is formed. This is usually allowed to stand spread out on a stainless steel plate to complete plasticizer absorption. This technique can also be used to dissolve solution grades of PVC in active solvents, to add stabilizers to such solutions or to PVC latex, and to prepare clear plastisols and organosols. In itself, wet blending will generally not yield good dispersions of filler in such systems, but can be followed with high-shear equipment such as a Cowles Dissolver. On a laboratory scale, small batches can be prepared using a food blender or similar device.

Very small batches (100–500 g) can be made, for example, to evaluate experimental new additives, in sigma blade mixing heads for torque rheometers, either by dry or wet blending methods. Alternatively, such equipment can be used to prepare concentrates of experimental additives for incorporation using larger-scale equipment.

18.3 PREPARATION OF FLUXED COMPOUND

Two-Roll Mill Laboratory preparations of dry blends are usually fluxed and converted to sheet form using a heated two-roll mill. Mill roll temperatures range from 165–175 °C for flexible PVC to 180–195 °C for rigid compounds. The milling procedure is described in ASTM D 3010. Although the latter suggests a roll speed ratio (friction ratio) of 1.3 to 1, ratios of 1.1–1.2 to 1 are often found more convenient for the operator. The rolls are most often heated with circulating fluid provided by constant-temperature devices, such as supplied by Sterlco. It is preferable to use a two-zone unit so that the front roll can be maintained about 5 °C warmer than the back roll. This will tend to keep the batch from jumping from one roll to another, as will using a modest friction ratio. ("Friction ratio" derives from a process where a soft compound is forced into fabric in the nip between two rolls operating at different speeds.) The mill must be vented in accordance with regulatory codes.

The first step in operating a laboratory mill is to check that the safety (an electromagnetic brake that stops mill roll motion instantly) is functioning properly. This device should never be used in place of the on–off switch to stop the mill other than in an emergency or test. The mill rolls and the mill pan beneath them are then checked for dirt and contaminants. It is preferable to use a clean stainless steel mill pan to catch droppings from the batch than sheets of kraft paper or polyester film. The latter will occasionally be caught up in the batch, ruining the investigator's efforts. The roll temperature is then checked with a contact or infrared pyrometer, the latter being more convenient and durable. The mill should be running while heating to provide a uniform surface temperature.

The mill is then stopped and enough of the batch loaded into the nip, set to paper-thin tightness, and allowed to warm for 1–2 minutes. The mill is turned on, and, with proper temperature settings, fluxed or semifluxed compound bands on the front roll. After all the batch has been banded, the operator, equipped with lint-free gloves, adds any part that has fallen into the mill pan, resets the nip to 1–5 mm (as is found most convenient), and then crosscuts the batch to insure uniform distribution. A laboratory mill knife should be used, of a grade of steel softer than the mill roll surface, such as supplied by Hyde Knife Co. and others, rather than with makeshift tools such as a linoleum knife or brass spatula. The operator should be instructed that if the mill knife falls into the batch, the action to be taken is to activate the safety brake rather than to try to retrieve the knife. The milling operation after fluxing should be completed in a set time (e.g., 2 minutes), for batch-to-batch consistent heat history. If a further ingredient is to be added, for example, a color concentrate, 2–5 minutes may be required. Finally, the mill nip is reset to the desired sheet thickness for testing. With most compounds, it is easier to turn off the mill to remove the batch. A cut is made across the surface, and, holding the cut end in one gloved hand, the operator turns on the mill and removes the batch. With very soft compounds, it is useful to use both hands and have the mill turned on by another. The batch is then allowed to cool on a stainless steel plate.

Internal Mixer If a series of batches are needed, it is convenient to flux the dry blend in a laboratory-scale internal mixer, such as a Farrel Banbury® or similar equipment available from Kobelco, Pomini, and others. The Farrel Model B Banbury® requires 1–1.5 kg of compound, depending on its specific gravity. Thus often a base compound is prepared in such a quantity, and several levels of the additive whose action is to be studied are then added to 200–500 g portions on a laboratory mill. Alternatively, for large-scale laboratory studies, a laboratory mill capable of handling a Model B batch of PVC compound (with 18 or 24 in (48 or 61 cm) rolls) is used. It is also possible to find a reconditioned Midget Banbury®, a benchtop mixer with a capacity of 350–500 g of PVC compound (this size is apparently no longer produced). The internal mixer must be heated, with either steam or circulating fluid. Rigid PVC compounds are mixed to 175–195 °C, flexible to 160–170 °C, depending on plasticizer level. The batch is dumped manually to a clean pan that fits beneath the drop door of the mixer, and is then transferred to a preheated two-roll mill for sheeting for test pieces.

An excellent use for the laboratory-scale internal mixer is in preparation of blends of PVC with rubbery polymers such as NBR and certain polyurethanes. Here, the entire batch may be mixed in one cycle. In many cases, all solids can be charged initially (with the rotors turning), and as the batch comes together, liquid ingredients added. Alternatively, a PVC/NBR masterbatch (with stabilizer and often with plasticizer) can be prepared, then cut into strips for further compounding with fillers, pigments, and additives of interest. For pilot plant studies, a #1 Banbury® with a capacity of 15–20 kg is useful.

Pelletized Compound At one time, pelletized compound was prepared in the laboratory (and in production) by feeding a strip of fluxed compound from a mill or laboratory extruder into a dicer, which, depending on the arrangement of the cutting knives, produced cubical or hexagonal cut pellets. These do not convey as efficiently or extrude with the output of more or less spherical pellets, and are, therefore, now uncommon in production. Since the entire point of preparing pellets in the laboratory instead of working with milled sheets is to simulate factory processing, there is little point in continuing with dicing equipment in the laboratory. It is possible, at least in some cases, with experience to correlate laboratory processing of diced pellets with factory use of spherical pellets. On balance, however, considering factors such as the intense noise pollution that is involved, laboratory dicers are rarely worth the investment.

Most laboratories that prepare pellets of PVC compound now use either single- or twin-screw extruders. With the former, strips of fluxed compound are fed to a laboratory extruder, such as are often supplied with torque rheometers, and extruded as round strands cut by a rotating knife against the face of the die. They are, therefore, referred to as “strand-cut” pellets. With such pellets, strand diameter is constant but length varies somewhat depending on the time elapsed before being cut by the rotating knife. As with diced pellets, they are useful in predicting plant only approximately (other than if production also uses strand-cut pellets).

Most pellets are produced in production using a twin-screw extruder. Laboratory models, such as the ZSK 30 (Werner & Pfleiderer) are available. These can be equipped with stuffing devices to force dry blend into the feed zone. A variety of screw designs are available in order to simulate factory conditions and for developing processing improvements. Generally, pellets are hot-cut from multiple holes in the die by rotating knives, yielding more or less spherical pellets of a relatively narrow size range. They are not as spherical or uniform as pellets produced in the factory using “underwater-cut” pelletizers, where the die cutting action occurs under hot water, facilitating formation of spheres. On the other hand, few organizations can afford the investment involved in miniaturizing such equipment.

Dispersion and Contamination Visual or microscopic examination is employed to evaluate dispersion and to discover gel particles and contamination. In the procedure outlined in ASTM D 3015, samples are pressed between glass slides on a hot stage at 10–25 × magnification and (usually) dark-field illumination. Because of the small sample size, it is often preferable to examine a thin-milled sheet visually. Gels will appear as clear spots in filled compounds. A useful test for resin gel content is to add 2–3 percent carbon black (e.g., GPF or FEF) on a laboratory mill (a black concentrate can be used) and to count clear gels per area. This is commonly run on PVC/NBR fluxed blends as a check for adequate mixing.

Examination of clear compounds often makes use (where rheology permits) of blown film samples. Although involving equipment expense and set-up time, the technique makes any defect obvious. With filled compounds, extrusion through screens is commonly used to check for contamination and poor dispersion (gels will tend to "swim through" screens). Fourier transform infrared (FTIR) spectrophotometers equipped with laser microscopes can often identify specks found on screen packs. It should be noted that these can derive from degradation during extrusion as well as from poor dispersion; thus, control samples are necessary. FTIR identification will often distinguish among contaminants, undispersed ingredients, and reaction products of degradation (e.g., chlorinated stabilizer residues).

18.4 MEASUREMENT OF THERMAL STABILITY

Dynamic Stability Dynamic stability tests indicate the resistance of the compound to a combination of heat and shear. They are highly useful in predicting processability in extrusion, calendering, and injection molding. The equipment used most frequently is the torque rheometer, such as supplied by C. W. Brabender and Haake, Inc. Dynamic stability measurements with a torque rheometer are covered in ASTM D2538. In this type of equipment, counter-rotating rotors (resembling internal mixer rotors) are driven in a mixing head with the back torque exerted by the batch measured by strain gauges with output to a computer screen. (Older models used mechanical dynamometers instead, with a much lower signal-to-noise ratio in output to a strip-chart graph.) The output is readily stored by the computer or sent to a network. Most models are now heated electrically with close temperature control (equipment heated by circulating fluid is still in service and quite useful, other than the hazard of occasional leakage of hot oil). Batch temperature is also recorded, and displayed on the computer screen.

The batch, either dry blend, pellets, or strips cut from a milled sheet, is fed into the head. Batch weight depends on specific gravity. With a mixing head rated at 60 g, commonly 60 g is used with clear and slightly filled compounds, 65 g with a variety of flexible compounds, 70 g with highly filled compounds. Often, pellets and dry blend are loaded with the rotors turned off; cut strips must be loaded with the rotors turning. After loading, the mechanical ram is lowered and the rotors (if not already running) turned on. There is varying opinion on whether to leave the ram down on the batch after fusion or not. If down, the process is less aerobic and considered a closer simulation of extrusion. Running with the ram open is probably a better simulation of calendering. It also provides for visual inspection. The ram can be replaced with a (usually home-made) device to collect volatiles evolved from the batch for analysis.

In testing for processability and color hold under high shear, rigid PVC compounds are typically run at 60 rpm rotor speed, flexible compounds at 90 rpm, at 190 °C. This readily permits estimation of fusion time, the peak torque reached as frictional heating and shear produce fusion. When torque levels off, small samples are periodically removed after various periods of time, for example, 5, 10, and 15 minutes, and so on. (Note that the rotors are turned off while retrieving samples.) Samples are most easily obtained with thin-nosed pliers from the section of the head between the rotors. Often, the maintenance department can be persuaded to weld a small, flat receptacle to the pliers so as to obtain attractive cartouche-shaped specimens. These are typically mounted on a chart side by side with control samples and other variations. The samples should be large enough (e.g., 0.5 cm × 1.0 cm) to permit measurement with a colorimeter. When a process is in good control, product should correspond to the first one or two rheometer specimens, perhaps the 5-minute sample. Normal excursions in the factory should correspond to the next two or three samples. In other words, the first few samples should show essentially no change in color.

Another observation to be drawn after fusion is the extent to which torque (i.e., viscosity) remains flat. A general drift downward (from some extent of chain scission) or upward (from slight crosslinking) is an indication of potential instability in extrusion or calendering. With passage of time, inevitably the samples withdrawn begin to show color formation. These should be analyzed closely as to changes in the components of ΔE, not just the overall color change, in order to deduce modifications to the formulation. (With black or dark-colored compounds, only the curve of viscosity versus time is obtained.)

Eventually, all samples will darken and torque will rise as crosslinking and resinification sets in. It is important to note whether the sample fails gradually or abruptly. A gradual mode of failure can often be induced by inclusion or increased level of acid absorber, such as zeolite or hydrotalcite. One should also note the appearance of discrete dark spots in a lighter matrix prior to failure; this may indicate too high a level of uncomplexed zinc in the compound. Once the batch turns dark, it is best to discontinue the test and immediately clean the mixing head. It is important to have a vent over the mixing head and it is suggested that the electronic components of the torque not be stacked upstream of the mixing head to prevent damage to circuit boards from hydrogen chloride gas.

In some sectors of the industry, it is common to run dynamic stability tests at 205 °C, with rotors at 100 rpm. This of course cuts the time needed for the test. In some cases, such as extrusion of commodity wire coatings, it may even be representative of production conditions and, therefore, of value in quality control. In most cases, however, such over-acceleration detracts from the diagnostic value of dynamic stability testing in evaluating ingredient addition or comparison.

In any program of additive evaluation, duplicate determinations of dynamic stability should always be run. The samples removed during the test, typically mounted on chart paper, should be stored in plastic folders and not exposed to light if to be used in the future as controls. All comparisons should be made with the same mixing head in the same torque rheometer; different pieces of equipment and different extent of metal wear will generate minor variations. When equipment is replaced or mixing heads reconditioned, standard formulations should be prepared to establish new controls. Instrument life is greatly prolonged by care in cleaning. A number of purge compounds for use with PVC residues are available. These are typically palletized stiff acrylic compounds with a great deal of resistance to decomposition. After completing a dynamic stability test, the head should be opened and as much of the contents taken out as can be easily removed. The mixing head is then replaced and filled with purge compound, the ram is lowered, and the rotors are turned on.

After fluxing, additional purge compound is added as needed. The head is then opened and the contents removed. At this point, minor hand cleaning with soft brass brushes should remove any residue, particularly if care has been taken not to allow the test batch to resinify completely. The rotors are removed and the shafts, if necessary, cleaned. On re-assembly, a second purge batch is often run to complete cleaning. With practice, these operations can be carried quickly.

Dynamic heat stability is often measured using a two-roll mill instead of a torque rheometer to simulate aerobic processing, typically calendering. A previously prepared batch is banded on the mill, usually with both rolls set at 190 °C. After various time intervals, often every 5 minutes, small samples are cut from the center of the batch, cooled, and mounted for determination of color change, ΔE, and its components. With robust compounds, that is, those strongly stabilized, there is often good correlation between torque rheometer and mill dynamic stability. With marginally stable compounds, the correlation may be quite poor.

Dynamic stability is also determined by use of a capillary rheometer, particularly for injection molding, where the high shear rates exceed practical measurements with equipment that essentially comprises a mixing system, such as a two-roll mill or torque rheometer. Most capillary rheometer usage is, however, directed to flow rate measurement, under which the procedures will be discussed.

Static Heat Stability In processing that does not involve high shear, such as with plastisols, latex, and solution coatings, stability is generally predicted by means of static heat stability tests. Two types of test equipment are in use. One employs a forced-draft oven equipped with a slowly rotating turntable; testing is described in ASTM D3012. The other, now more common, uses a recirculating-air oven, with rate of recirculation per ASTM D2115. With both procedures, the oven exhaust should be vented. In either case, the results have comparative value only and control samples must be run. Small squares are cut from a milled sheet and placed on aluminum or steel trays for oven exposure at temperatures ranging from 175 to 200 °C. After set periods of time, a sample from each variation is removed, cooled, and evaluated for color change. It is important to use a set number of samples in each test and to distribute these evenly in the oven. Oven aging of 50 samples will typically yield less discoloration than the same test using 5. Static heat stability is often used for QC purposes, because a large number of samples can be tested quickly. For effective product development, both static and dynamic stability tests should be run. With robust (strongly stabilized) compounds, results are often comparable. When this is not the case, the results are commonly found to predict different orders of stability.

In a variation of static heat stability, the samples are exposed as above, but at lower temperatures, such as 100–150 °C, for periods of weeks. This procedure, referred to as “long-term” or “low-temperature” heat aging, is used to predict service life, typically of flooring or wall covering components. The mechanism of degradation may differ from that in high-temperature static heat stability; thus, results may be far different.

Static heat stability measurement has been automated with a device called the Metrastat® (supplied by Dr Stapfer GmbH of Dusseldorf). In this equipment, several strip samples move at an adjustable rate into and through an oven at preset temperature. After exposure, the strip can be checked for discoloration versus time of exposure, stored as the entire strip, or cut into sections for mounting (as with individual specimens from an oven). This enables other laboratory operations to be run simultaneously without the hazard of omitting to take samples from the oven inadvertently. Auxiliary equipment is available from the supplier to monitor hydrogen chloride evolution and to check for development of fluorescence in the sample (from formation of conjugated unsaturation, typically a precursor to appearance of visible discoloration). This versatility makes the Metrastat® an excellent compound development tool. Determination of fluorescence is the subject of ASTM E 1247.

Chemiluminescence Chemiluminescence (CL) was previously of interest as a means of measuring ozone level in the atmosphere (ASTM D 5149). Excited species from the reaction of ozone with ethylene produce a luminescent effect that can be measured with special purpose equipment (Chemilume® CL400, Atlas Instruments). This technique has been used by Billingham and Kann to follow the degradation of PVC from the radicals produced by reaction of oxygen with unsaturation formed from loss of hydrogen chloride, and to evaluate the effectiveness of stabilizers. In their experiments, most completely presented in the PhD thesis of Yelena Kann (University of Sussex, U.K., 2003), CL was observed in the oxidation of a model unsaturated compound, β-carotene. It was then found that the pattern of CL emission during PVC degradation correlated with that of discoloration (ΔE). Although heretofore of interest mainly to workers interested in the mechanisms of polymer degradation, the CL technique should be of interest to the formulator, since it tracks events early in the response of PVC compounds to heat, shear, and oxidation—precisely the timescale appropriate to processing.

18.5 MEASUREMENT OF FUSION AND MELT FLOW

Fusion The time needed for fusion under heat and shear is measured with both pelletized and dry-blend compounds. In extrusion and injection molding applications, it is desirable to be able to predict fusion speed in the extruder and the extrusion feed section of the injection molding machine. Most often, such measurements are carried out with a torque rheometer at a temperature corresponding to the heat setting of the fusion section of the extruder barrel (as described in ASTM D2538). With pellets and with rigid PVC dry blend, the rheometer output typically shows a brief delay as frictional heat builds, followed by a strong increase in torque as fusion proceeds, then a decrease to melt viscosity at that temperature, eventually followed by an increase in torque as the safe processing window is exhausted and degradation begins. With rigid PVC compounds run at high output, such as siding and profiles, the processing window is often quite brief because the stabilizer level has been adjusted downward to the lowest level at which an acceptable product can be extruded. In the long term, it is best to find this point and then use 10–20 percent additional stabilizer to accommodate occasional excursions from ideal extrusion behavior. Over time, this will be found to yield lower total cost than production with the lowest possible stabilizer level. (Similarly, long-run lowest-cost will result from line speeds slightly less than the maximum output of the extruder.)

The delay time before fusion begins should correspond to the time of residence in the feed zone of the extruder. With dry blend, it is usually controlled by adjusting the balance of calcium stearate fusion promoter versus external lubricant. With pellets, it is influenced by pellet shape and size, as well as by the presence on the surface of external lubricant or pellet antistick agent. Since, with pellets, these factors are typically only subject to minor adjustment, recourse is usually to variation of feed zone temperature.

Some flexible PVC compounds show delayed fusion; that is, there is a secondary increase in torque following the peak from frictional heating. This behavior is generally undesirable; late fusion in the extruder barrel can cause rough extrudate and limit output. The problem can be approached with a higher temperature profile (and typically higher level of stabilizer) or by revising the plasticizer(s) towards higher resin compatibility. It should also be noted that problems of this type (trying to process the lowest possible cost compound at the highest possible output) often have engineering rather than formulating solutions; that is, it may make more sense to modify the equipment as well as, or rather than, the compound. Finally, it should be appreciated that prior heat and shear history affects fusion. When the rate of fusion is found to be inadequate in processing, experiments should be run to determine whether a decrease in heat and shear input during mixing might not be useful.

Compound fusion has also been measured with other types of equipment, notably with capillary rheometers with short dies ($L/D < 1$). With such devices, referred to as "zero-length dies," the pressure required to extrude a given quantity of compound is related to the degree of fusion. Cone–plate and parallel plate rheometers can also be used. All of these are primarily research tools for the development of new additives; the formulator in the field almost always relies on the torque rheometer.

Melt Flow In most thermoplastics, melt flow is determined using the melt index apparatus per ASTM D3364. In this method, a ram of given weight forces compound in a heated barrel through an orifice of given dimensions, the orifice being opened after a given preheat time, typically 3 minutes at 175 °C. In Method A of the specification, flow through the orifice is reported in mg/min. In Method B, the time for the ram to drop a given distance is converted, using the compound's specific gravity, into output in g/10 min. Although it is the method most commonly used for heat flow measurement with polyolefins, melt index is no longer widely used with PVC compounds. The test is greatly influenced by heat and shear history of the sample, compound stability, and extent of lubrication. It tends to yield poor precision, and has been largely replaced with more sophisticated equipment.

Melt flow in extrusion can be determined using a torque rheometer, such as supplied by Brabender and Haake, equipped with a laboratory extruder in place of the customary mixing head. Various screw designs are available, corresponding (at least roughly) to those used in production extrusion of rigid and flexible compounds (although with fewer heating zones). These are typically of $\frac{3}{4}$ in (19 mm) diameter. Back-torque on the screw is measured with strain gauges. Head pressure is also determined. A rod or variable-thickness tape is extruded. Crossheads are also available to simulate wire covering processes, with conductor unwind and product take-up arrangements. This type of equipment is excellent for comparison of one batch with another, and, in experienced hands, can be used to predict production performance. With either rod or tape configuration, the quality of the extrudate can be assessed. This has led to frequent use, particularly by suppliers of mixed compound for extrusion. Poor dispersion is easily spotted. Extruded tapes can also be used to die-cut samples for physical testing (in place of molded sheets).

In a variation of the above, the extruder head of the torque rheometer is fitted with a capillary die, often with three orifices of different L/D characteristics. These can be used to estimate capillary length corrections, thus approaching a measurement of true viscosity, independent of equipment characteristics. Such equipment is more useful than a melt index apparatus for measurements at high shear rates corresponding, for example, to injection molding. The technique is limited by the basic capability of the torque rheometer and experimental difficulties, notably the tendency to exceed the strength of shear-limiting pins in the drive section at high shear rates, and has been largely superseded by the use of automatic capillary rheometers.

Computerized capillary rheometers are supplied by Haake, Instron, Dynisco, Bohlins, and others. Models are available with corrosion-resistant capillaries suitable for use with PVC compounds. Viscosity versus shear rate and shear stress can be determined over a huge range of shear rates at a particular temperature as compound is driven through the capillary. Correction factors for capillary entrance and length effects are applied automatically by equipment software. The length of extrudate of good appearance at accelerated temperatures can be taken as a measure of stabilizer effectiveness at a given shear rate. Thus, a compound can be evaluated for performance in a number of processes. Capillary rheometers are typically used by suppliers of resins, additives, or mixed compound.

Viscosity versus shear rate and shear stress can also be determined at various temperatures with automated cone–plate or parallel plate analyzers, such as supplied by Rheometrics and others. Typically, a sample is subjected to a sinusoidal oscillating strain and the resultant torsional force measured. Strain gauges lead to output of elastic modulus, loss modulus and tan Δ. These can be obtained over a wide frequency range at a given temperature, or over a broad temperature range, showing first- and second-order transitions. Typically, the equipment is quite expensive.

18.6 DETERMINATION OF PHYSICAL PROPERTIES

Molding Test Sheets Although it is possible to measure physical properties on milled or extruded samples, the most consistent results are obtained by molding dense test sheets using a hydraulic press equipped for both heating and cooling, such as supplied by Carver, Pasadena Press, and others. The most common configuration uses electric heat and water cooling; older units may use steam–water combinations. Circulating oil systems do not provide rapid enough temperature transition for use with thermoplastics. An important feature of suitable presses is that two-handed operation is required such that the press cannot be closed while, for example, adjusting the position of the mold. Most modern presses provide adjustable automatic cycling and can accommodate four-cavity molds (per ASTM D2287). The press is typically set at 190–200 °C for a heating cycle of about 5 minutes, followed by cooling under pressure to 40–50 °C. Molds should have corrosion resistant, high finish surfaces.

Commonly, instead of a mold, the sample is placed between two rigid stainless steel sheets, using a spacer, for which the jargon is "picture frame." This simple and inexpensive technique avoids surface defects from shrinkage during cooling. The sample to be molded should be slightly thicker than the spacer frame and slightly smaller in area, overall 5–10 percent greater in weight than the molded sheet. Weighing the sample to be molded is good practice. The direction of milling should be noted (generally on the specimen after molding). The extent of differences between machine and cross-direction properties can be useful in formulating for various applications. For example, if the difference is large and not highly variant with fusion conditions, it may suggest investigation of filler blends of different aspect ratios.

After removal from the press, the mold or picture frame sandwich is allowed to cool before opening (using brass implements). It is, therefore, useful to have several picture frame molds of comparable dimensions. The best precision in physical property measurement is obtained by allowing the molded sheet to relax at room temperature for a set period of time, often 24 hours. After opening the mold, the sample should be observed for evidence of surface bleed from excess external lubricant. (With compounds intended for metal adhesion, it may be necessary to use an external mold release coating. Those based on PTFE are effective with vinyl compounds and tend not to interfere with subsequent testing. Silicone-based mold releases, if used, should be of the type that is heat-cured to the mold, rather than migratory.)

Stress–Strain Measurements Samples are cut from conditioned molded sheets (ASTM D618), usually in the form of dumbbells, having a narrow section of 0.25 in (6.4 mm) (0.125 in (3.2 mm) in some cases). Dumbbells are best cut using a hand-operated arbor press of 1–5 ton capacity, such as supplied by Dake, Famco, Greenerd, Janesville Tool and others, the piston driving a hardened steel die of the correct dimensions (ASTM D638). An ordinary HDPE cutting board provides a suitable cutting surface that will not damage the die edges. More commonly, a leather-coated steel maul is used manually to drive the die through the sample against a butcher block surface. This procedure causes occasional nicks to the sample and reduces precision. In all cases, the samples are examined for incidental damage before use.

With most other thermoplastics, samples for tensile testing are injection-molded directly to the desired shape. This can also be done with many PVC compounds. Since the edges of samples prepared in this manner tend to have fewer microcracks than with die-cut samples, failure is often at higher values of tensile strength and elongation. As the results are usually intended for comparison, either method is appropriate as long as followed consistently.

The maximum load sustained by the sample during the test, divided by the original cross-sectional area, is referred to as the *ultimate tensile strength*. Since at that point, the sample obviously no longer retains its original cross-sectional area, the measurement is of *apparent* ultimate tensile strength. In some cases, the stress–strain curve is a simple upward line from zero to tensile strength (stress at rupture) at the corresponding strain, the *ultimate elongation*. This is typical of many filled compounds. If the polymer chains are able to orient under load, the initial upward stress–strain curve may be followed by a yield point, where the oriented composition accepts increased strain. Stress at the yield point is referred to as the *yield strength* (again an apparent rather than true value). Many flexible compounds behave in this way. In some cases, after the yield point, the measured stress goes through a maximum (tensile strength) and then declines somewhat before rupture, at which point it is referred to as *breaking strength*. Stress at particular values of strain prior to rupture are referred to as, for example, *100 percent modulus*. Such moduli are also apparent rather than true values. Stress values are now generally reported in SI units: megapascals (MPa) rather than in psi or $\mathrm{kg/cm^2}$. Extrapolation of the initial linear section of the stress–strain curve to the point of failure leads to an *apparent* value of the modulus of elasticity (Young's modulus) of the composition (ASTM D638).

It is important to record the entire stress–strain curve. If one sample follows the curve set by a number of others but fails to travel the average length, that is, is low in tensile strength and elongation, the break point should be checked for evidence of poor dispersion or other defect. If there is failure of the stress–strain curves of a number of samples to follow a common track, the homogeneity of the composition is suspect. The experienced technologist can often estimate the utility of a new compound for a given application by inspection of its stress–strain curve.

The tensile properties of soft flexible compounds having high ultimate elongation can be determined readily with mechanical as well as automated testing equipment. With rigid compounds, sophisticated analyzers are used, measuring strain with displacement transducers or noncontacting extensometers. Equipment is supplied by Instron, Ametek, Admet, Benz, Thwing Albert, and others.

Hardness Measurements The hardness of flexible PVC compositions is usually given using the Shore A and D scales; rigid PVC with the Shore D and Rockwell R scales. In the Shore procedure (ASTM D2240), a calibrated spring records the force needed to indent the sample with a blunt probe of specific dimensions, the Shore A probe being blunter and Shore D probe more acute. Measurements are affected by temperature variation, rate of application of the strain, and elapsed time before reading (the contact time). Contact time, 15 s per ASTM, should be recorded. Values also tend to change with time after sample preparation from orientation to relieve strain. The precision of the measurement is often overstated.

Procedure B of the Rockwell R hardness test (ASTM D785) applies to plastics. The load on a 0.5 in (1.3 cm) indenter is held for 10 s at 10 kg and then increased to 60 kg. After 15 s, the increase in depth from the 10 kg (minor load) to the 60 kg (major load) is measured. The sample is then inspected for cracking. In experienced hands, the measurement can be used to assess ductility or brittleness of rigid PVC compositions.

Flexural Strength Structural capability is more realistically tested by measurement of flexural, rather than tensile strength, since few failures occur in tension. Flexural modulus, per ASTM D790, reflects the resistance of the composition to a force perpendicular to its longitudinal axis. Testing is carried out with an automated tensile/compression tester, such as supplied by Instron and others. Two methods are used. In Method 1, a three-point system is used. Brittle failure occurs at the point opposite the load. Method 2 uses a four-point system. Load points are spaced so that maximum stress is developed at the center. When a specimen does not fail at the maximum stress point using Method 1, Method 2 should be used. (When failures are found at locations other than at the point of maximum load, the failure point should be examined for evidence of poor dispersion.) If failure is anticipated with a small deflection, a deflection speed of 0.01 in/min (0.25 mm/min) is used (ASTM Procedure A). With failures at larger deflections, this is increased to 0.10 in/min (2.5 mm/min).

Stress and strain at failure are readily calculated from the sample geometry in both cases. If failure has not occurred with 5 percent deflection strain, this is usually reported as the flexural yield strength. In practice, results depend on the heat history of the sample, extent of fusion, uniformity of dispersion, and freedom from surface cracks. Generally, molded specimens yield higher values than those die-cut from pressed sheets or actual articles of commerce.

Instead of attempting to assess the resistance of a composition to a flexural strain by accelerating the amplitude of the strain, the frequency of deformation can be increased. Miniaturized versions of the three-point and four-point apparatus of are used in dynamic mechanical analyzers, such as supplied by Rheometrics and others. Flexural modulus can be determined versus frequency over a broad temperature range, before and after heat aging or service in the field. Procedures are covered in ASTM Publication STP1402.

Tear Strength Tensile testing equipment is used routinely to determine tear strength, with samples die cut per ASTM D1004 for un-nicked specimens and ASTM D1938 for those with prescribed razor blade nicks. The latter test is run at a crosshead speed of 10 in/min (25 cm/min), the former at 2 in/min (5 mm/min). These tests are sensitive to orientation and to microcracks made in sample preparation. Other factors being equal, tear strength will increase with increasing molecular weight.

Low-Temperature Brittleness Low-temperature brittleness is most often determined using the brittle point apparatus of ASTM D746. Typically, five 1.5 in × 0.25 in (38 mm × 6.4 mm) die-cut (or molded) specimens of 0.075 in (1.8 mm) thickness are clamped in the apparatus at one end by bolts tightened to a constant torque. The apparatus is placed in a low-temperature bath, commonly silicone fluid, and held for 3 minutes after the test temperature is reached. They are then impacted with a specified cutting blade moving at 6–7 ft/s (1.8–2.1 m/s). Failure is defined as a crack visible without magnification, or complete division into pieces. The test is repeated at various temperatures, usually with a total of 10 samples at each temperature. Most commonly, the brittle point is taken as the temperature at which 5 of 10 samples fail. The test is notoriously sensitive to sample preparation and to operator technique. It can be used for QC purposes, but is only a crude predictor of service properties.

Low-Temperature Flexibility In the procedure of ASTM D1043, 2.5 in × 0.25 in (64 mm × 6.4 mm) samples of 0.04–0.125 in (1.0–3.2 mm) thickness are subject to torsional forces at low temperatures and extent of recovery measured. A modulus of rigidity can be calculated. The problem with torsional recovery, as with brittle point measurements, is not merely imprecision. Neither method considers that the response of a polymeric composition depends not only on temperature but also on the rate at which the load is applied and the frequency. Elastic and flow response are more reasonably determined by dynamic mechanical thermal analysis (DMTA), which yields a plot of elastic and loss moduli versus temperature over a range of frequency. This is of much greater utility in predicting service behavior and in part design. For example, a part may lose elastomeric character at a particular low temperature but be in a configuration where this does not cause failure. In other cases, service may be such that the glass transition temperature (T_g) should not be approached. T_g is constant only as (an often bad) first approximation. It is dependent on ΔT (rate of temperature change) and ΔP (rate of loading). Thus, the measurement is more predictive if obtained over the range capable with DMTA.

Heat Distortion Resistance Flexible PVC compounds can be tested per ASTM D2633, in which a dial type thickness gauge is preheated at 121 °C for 1 hour, and then a sheet sample inserted for a second hour with a 2 kg load on the gauge. This is basically a creep test. The percent change in thickness is taken as the heat distortion, ignoring effects of thermal expansion and shrinkage from orientation. The test has limited value except in direct comparison of samples.

Rigid PVC compounds have been characterized by Vicat Softening Point per ASTM D1525. This test measures the temperature at which a flat-ended needle of 1 mm^2 cross-sectional area will penetrate the sample to a depth of 1 mm under a load of 1 kg. Flat samples are heated at either 50 or 120 °C per hour. This test is also of limited value.

For many years, heat deflection under flexural load (HDUFL) testing followed ASTM D648, using a three-point apparatus. The deflection temperature is taken as that at which a deflection of 0.010 in (0.25 mm) is caused by the application either of a 66 psi (0.46 MPa) or a 264 psi (1.82 MPa) stress load. This procedure has been revised in ASTM E2092 so as to use DMTA with a three-point fixture. The data are infinitely more useful, but do not necessarily correlate with results using D648.

E2092 using DMTA is the best current procedure for evaluating additives for improvement of heat deflection resistance. These are generally PVC-compatible polymers of higher heat distortion resistance (higher T_g), which have a more than proportionate effect in reducing flow under load. That low levels of certain species have the ability to restrict flow at points of stress is not surprising; they are the reverse of, but analogous to, internal lubricants. It might be supposed that an additive that restricts flow under load might obstruct processing. This is not usually the case with heat distortion improvers; in fact, some are also processing aids. This results from mixing and fabricating involving much higher shear rates than flow under load. Viscosity versus shear rate curves often show crossing at the extremes. Where successful resistance to a rapidly applied load requires ductility, as in some impact resistance tests (see in the following), additives that are heat distortion improvers can have a negative effect. Thus, their use is often accompanied by an increase in the level of impact modifier.

Impact Resistance Both flexible and rigid compounds can be tested by Gardner impact, ASTM D4226. The method measures the height from which a 3.6 kg dropped weight of specified geometry causes failure in a flat sheet of given dimensions. Failure includes any cracks, holes or visible tears in the specimen. The height at which 50 percent of the specimens fail is typically reported. Rigid PVC samples usually fail in a brittle mold; flexible PVC samples at room temperature tend to show ductile failure.

In a variation of this method (ASTM D3029), a free-falling 30 lb (13.6 kg) dart of specified dimensions is used and the height needed for failure determined (mean failure height), or a standard height (26 in, 0.66 m) is used and the weight of the dart (mean failure weight) needed for failure determined. In the specification, the dart is also referred to as a "tup," presumably from well-drilling jargon.

The most common test for impact resistance of plastics is the Izod pendulum method, ASTM D256, often used with rigid PVC. In this method, either the mass of the weight or the extent of arc can be used to specify failure. It is differentiated into notched and un-notched Izod: the former, notably more severe, uses a sample with a cut notch of specific dimensions. With suitable instrumentation, Izod measurements can be extended to determination of low-temperature impact resistance.

Typically, Gardner and Izod measurements have poor correlation, the former tending to be more influenced by ductile behavior of the composition. They are, nevertheless, both useful in comparing samples and in estimating the usefulness of impact modifiers.

18.7 DURABILITY TESTS

Weathering Resistance Prediction of service life, although one of the most important areas of testing, is probably the most uncertain. Cable jackets of synthetic rubber used in the Distant Early Warning (DEW) Line in Northern Canada in the 1950s were forecast to have a 20-year lifetime. Most are still in service. Similar synthetic rubber wire coverings were used at that time for automotive wire harness; when found in antique automobiles, they are immediately replaced. Such variation in service life is nowhere more evident than in outdoor weathering. Samples are typically exposed to natural aging in Florida and Arizona. Results may or may not correlate. Results in an industrial area of New Jersey can be worse than either of the above if the composition contains ingredients that react with oxides of nitrogen (amines, phenols, and additives whose hydrolysis yields phenols).

Samples are typically placed at a 45 ° angle to the vertical, facing South. The use of magnifying Fresnel lenses in front of the samples accelerates the effects of exposure, but these do not necessarily correlate with unmagnified exposure. A test device invented by DSET Laboratories uses mirrors to track the sun, to increase sunlight exposure (it is thought) by a factor of 7–9. When accompanied by a water spray cycle, the test machine is referred to as EMMAQUA. These various procedures are internally consistent and are reasonable to use in comparing samples. Their greatest long-term value to the formulator may lie in investigation of why there is poor method-to-method correlation. The variables involved may be more useful in compound design than any set of results.

After completion of outdoor exposure, samples brought indoors often increase in discoloration. This is an indication that the antidegradant system in use has been exhausted by the exposure and is unable to trap radicals that remain (and propagate). Revision of the antioxidant content, particularly in flexible PVC, the type and level of organophosphite, is indicated.

The effects of outdoor aging to the sample may include discoloration, gloss reduction, chalking, development of cracks or of a tacky surface, reduction of physical properties, shrinkage, and microbial growth. All of these can be checked, color change being among the most easily carried out. The most important cause of degradation is thought to be UV light exposure. (It should be noted that since the best hindered amine (HALS) light stabilizers are not as yet suitable for use in PVC with organotin mercaptide stabilizers, there is good reason to consider rigid PVC overcoated with a HALS-containing acrylic layer for outdoor applications.)

The most widely used equipment for laboratory simulation is the xenon arc Weather-Ometer® supplied by Atlas Electric Devices; procedures are described in ASTM D2565. Test temperature is adjustable, as are water spray, and light and dark cycles. Tests are commonly run to 500, 1000, and 2000 hours and samples are compared with controls. Another popular device is the Q-Panel® fluorescent lamp exposure apparatus (Q-Panel Co.). Similar cycles are run at accelerated settings of 50–70 °C, with or without water spray cycles, per ASTM D4329. The UV-A 340 fluorescent lamps closely simulate an average pattern of solar radiation received by the earth in the range of 290–360 nm, and are generally used. (It should be noted that there can be substantial deviation in incident solar radiation.) The xenon arc lamp also provides good simulation of what is taken as average solar radiation. The two methods nevertheless do not necessarily yield comparable results. Despite this, either may be used to compare samples and, in the hands of an experienced technologist, used to predict outdoor service capability. The samples tested are large enough to be used for measurement of physical property changes as well as discoloration. Xenon arc devices have been in service longer and have wide acceptance; the fluorescent lamp apparatus uses less space and is less expensive. The work discussed in the foregoing suggests that chemiluminescence (CL) measurements could also be useful in prediction of weatherability.

UV-B313 lamps do not simulate natural sunlight but rather strong UV light exposure at 275–340 nm, with peak intensity at 313 nm. UV-B lamps are a good choice in screening new additives as UV light absorbers or for conducting light-initiated reactions. With all UV light sources, UV-B lamps in particular, eye protection is essential.

Volatile Loss Determination of loss of volatile components of plastics is the subject of ASTM D1203. It is generally carried out only on flexible PVC samples. Method A uses direct contact between the sample and activated carbon at 70 °C for 24 hours. It is a measure of combined volatile and migratory loss. Method B uses a wire cage to prevent direct contact and migration, and is run at 100 °C. Both methods typically use samples 5 cm in diameter, most often 0.35 mm in thickness. Sample thickness greatly influences the result, thinner samples having greater percent loss of volatiles. Thus, sample geometry must be closely controlled. The test is of relative value in comparing compounds, but can be translated into service performance only with a great deal of experience.

Volatile losses from compounds are now almost always instead determined by thermogravimetric analysis (TGA). The methods are the subject of ASTM E 2105. Microsamples are heated at a standard rate in nitrogen, and progressive weight loss is determined with a microbalance. The evolved gases can be swept into an infrared spectrophotometer for identification, or into a cold trap for the same purpose. Suitable equipment is supplied by Perkin Elmer and by TA Instruments (among others). Alternatively, the evolved volatiles can be separated and analyzed by gas chromatograph–mass spectrometer (GC–MS) equipment. Thus, the formulator learns not just how much, but also which ingredients are volatile at various temperatures. TGA is routinely accompanied by differential thermal analysis (DTA), in which the energy input needed for weight loss is measured. DTA practice is covered in ASTM E537. Correlation of anticipated service conditions with DTA–TGA data can give the formulator a clear indication of fitness for service, as well as a variation-to-variation comparison.

Fog Testing A consequence of loss of volatile components can be their condensation onto cooler surfaces, such as from automotive interiors to the windshield. Test procedures have been issued by automotive manufacturers and through standards such as DIN 75201 and ISO 6452. Two methods are in use. In the gravimetric method, DIN 75201-G, a sample is heated in a beaker in a constant temperature bath at 100 °C for 16 hours, the beaker being covered by a preweighed sheet of aluminum foil. The weight gain often does not correlate with the gravimetric method of ASTM D 1203, but is likely to be consistent with the TGA procedure of ASTM E 2105.

In wider use in North America is the measurement per DIN 75201-R. The sample is heated to 100 °C for 3 hours in a constant-temperature bath, with volatile components condensed on a glass plate at 21 °C. The reflectance at a 60 ° angle is compared with that of control plates. A common piece of equipment for such tests is the Haake® P-2 Fogging Tester (Thermo Electron Corp.) Not only volatile plasticizers, but also many common ingredients, such as stearic acid, contribute to fogging. Low-fogging heat stabilizers are typically free of solvents and other low molecular-weight components and use relatively high molecular-weight phosphites. PVC components particularly likely to generate automotive fogging include plastisol and powder coatings, although inappropriately formulated articles of all types may contribute.

Loss of Physical Properties On oxidative aging, PVC is one of the classes of polymers that tend ultimately to crosslink, leading to decreased elongation and ductility. Oven aging is routinely used in formulating to compare samples, investigate the effects of additives, and establish conformation to the vast array of specifications based on resistance to such exposure. Oven aging of specimens is covered in ASTM D5510. Two types of oven can be used: convection and forced-air. Specifications of such ovens are the subject of ASTM E145. Most in use with PVC use rotating turntables. For precise results, it is important to use about the same total volume of samples in each experiment, with comparable distribution in the oven (even with a turntable). Exposure temperatures depend upon the specification in hand, and range from 70 °C to as high as 150 °C (for XL-PVC).

Underwriters Laboratories (UL) also issues specifications for PVC wire coverings; similar are issued by the Canadian Standards Association (CSA) and European organizations. UL Bulletin 1581 requires exposure for 7 (occasionally 10) days at specified temperatures, for example, 100 °C for THW wire (T = thermoplastic, HW = heat- and water-resistant). If after such aging, 65 percent or more of the initial elongation persists, the wire is, in this regard, suitable for being labeled THW, 90 °C service. One must recognize that the service rating is a comparative and approximate designation. If maintained perpetually at 90 °C in air, both conductor and covering would ultimately degrade. What is implied is that the construction could survive excursions to as high as 90 °C without decomposition.

It has in the past been popular to use heat aging data to forecast using Arrhenius analysis. The logarithm of the time needed for a diagnostic property (e.g., ultimate elongation) to decrease to a value arbitrarily chosen as the failure point at an elevated temperature is plotted versus reciprocal test temperature. This is extrapolated to the predicted service temperature, and the associated failure time is estimated. The method, the subject of the now discarded ASTM D2648, presumes a constant value of energy of activation for whatever processes are occurring. This is almost never true. Degradation mechanisms are sensitive to temperature and other variables. The tests leading to the Arrhenius plot are typically over-accelerated. Thus, the DEW line cables with a predicted service life of 20 years survived for more than 50. If it is necessary to supply such predictions as part of a specification, estimates may be made with infinitely less effort using DTA methods per ASTM E698.

UL 1581 also specifies retention of elongation after heat aging in ASTM No. 2 oil (a moderately aggressive fluid to which vulcanized elastomers such as Neoprene and

CPE are resistant). This fluid is now referred to as IRM 902, per ASTM D5964. Wire coverings rated for oil-resistant service at 60 °C per UL Class 12 are immersed at that temperature for periods of either 7 or 60 days, depending on the category, and expected to retain either 75 or 85 percent of original ultimate elongation. With other categories, testing may be at 75 or 100 °C. As with other service ratings, it must not be imagined that insulated wire so rated would withstand indefinite service submersed in hot oil. Thermoplastic PVC is not an option for oil-well drilling cables. The tests imply fitness for service in applications where hot oil contact would not have catastrophic results. In cases where performance is borderline, partial replacement of plasticizer with NBR is of considerable utility.

Consistent sample preparation is necessary for aging tests to be significant. For example, specifications generally do not require tensile/elongation specimens to be die cut before exposure (as is customary). Cutting the tensile specimens after aging a sheet sample tends to be less severe.

Extraction Tests Loss of plasticizer and other extractables can be measured using film or sheet samples in media such as mineral oil, natural oils, alcohol, or soap solution per ASTM D1239, typically run for 24 hours at room temperature. In the case of solvents, such as hexane, the solution may be concentrated for chromatographic analysis with infrared or mass spectrometer identification. The nature of the extractable fraction is as important to the formulator as the quantity, particularly in compound reconstruction (discussed in the following). Extraction of water-soluble species, such as dispersants in latex coatings, is carried out for longer time periods.

Exudation and Migration Historically, flexible PVC samples were suspended in closed (but vented) bottles above a layer of distilled water to generate 100 percent relative humidity and placed in a circulating air oven operating at 60 or 80 °C, per ASTM D2383. If such tests are run regularly, it is reasonable to invest instead in a constant temperature, constant humidity device. Such equipment is also useful for studies of biodegradation (ASTM D6954), and effects on rigid foam (D2126) and on electrical properties of wire coverings (D2305). Per D2383, after various periods of time, the samples are examined for visual evidence of exudation and rated (more or less subjectively) as showing none, slight (tackiness), moderate (thin film evident), or heavy (actual droplets).

Another subjective test is run per ASTM D3291, generally on wire coverings. Samples are clamped in 180° loops of 9.5-mm inside diameter so as to induce exudation under strain. In this case, after various time periods, the surface is wiped with absorbent paper and the extent visually estimated and compared with the behavior of control samples. In both tests, it is more useful to the formulator instead to remove the exudate with a small amount of hexane and determine by analysis how much of what has exuded.

Plasticizer migration is also the subject of ASTM D2134, in which flexible PVC is placed in contact with a surface coated with nitrocellulose lacquer for a specified time and temperature, measuring changes to the hardness of the nitrocellulose coating. It is generally more useful to use polystyrene, ABS or other surface more relevant to service conditions (other than to evaluate the suitability of a PVC surface for printing with nitrocellulose-based inks). Migration of plasticizer from vinyl fabrics is covered by ASTM D2199.

Staining of plastic articles is treated generally in ASTM D2299. With flexible PVC, stain most often results from solubility of the intrusion in the plasticizer. The number of plasticizer-soluble species that can discolor vinyl is large, ranging from petroleum products, inks, cosmetics, and food products to excretions of bacteria and fungi. Rigid PVC is more difficult to stain, but it is susceptible to pigments containing chromophores based on conjugated unsaturation, such as carotenoid pigments found on the airborne spores of certain fungi. The vinyl flooring and wall covering industry has developed a number of ad hoc staining tests of limited interest to general purpose formulation. In many cases, it is more useful to explore barrier coatings to prevent staining in preference to revision of the plasticizer content.

Abrasion Resistance Abrasion resistance of flexible PVC compounds is often a factor in applications such as footwear, cable jackets, belt covers, flooring, and automotive undercoats. The most widely used test is Taber Abrasion, ASTM D 4060. In this method, a standard abrasive wheel under a 1 kg load runs perpendicularly to a rotating 4 in (10 cm) disk sample. Weight loss per 1000 revolutions is measured, commonly to 5000 cycles. Note that ASTM regards D 4060 as having poor reproducibility and suggests it be used only internally. A variation using abrasive sandpaper, D 1242, has been withdrawn by ASTM, again from poor reproducibility. D 4060 and D 1242 results had notoriously poor correlation. In a related method applicable to clear samples, light diffraction in the abraded track is recorded (ASTM D 1044).

The problem with all of the above is that they are influenced as much or more (and, depending on the method, in different ways) by the coefficient of friction of the plastic surface as by its inherent toughness. Thus, a surface coating of external lubricant may, in practice, assist a building wire jacket in being dragged through holes in wooden joists, but, in the above test methods, act as a cutting fluid in promoting removal of compound by the abrading tool. In such cases, UL abrasion resistance requirements may hinder rather than assist development of the most suitable compositions. It is too early to state whether a new ASTM standard, F 735, which uses oscillating sand as the abrading medium, will meet with greater success. In general, abrasion resistance will increase with the molecular weight of the resin and with the extent to which fillers have reinforcing character. It is vastly increased by crosslinking. Performance in standard tests of abrasion resistance is often more influenced by choice and extent of external lubrication. This can be a problem when lead stabilizers are replaced with typically more lubricating mixed metal systems.

18.8 FLAME RESISTANCE AND SMOKE GENERATION

Limiting Oxygen Index One of the most widely used methods to estimate the flammability of a composition is to measure the minimum ("limiting") percent of oxygen in an oxygen–nitrogen mixture that will sustain combustion. Limiting oxygen index (LOI) is the subject of ASTM D 2863. Apparatus is available commercially, and results are easy to obtain and generally reproducible. LOI values of 27–30 usually imply success in small-scale horizontal flame tests; around 35, in vertical flame tests. All of these are good screening tests for initial evaluations and comparison with controls, but are only roughly predictive of behavior in the field. The problem is that, with increasing temperature, actual oxygen index decreases; that is, that with sufficient heat input and flame temperature, all C—H bonds will oxidize.

UL-94 Flame Tests In the UL-94 vertical flame test, a Bunsen burner having a 19 mm flame is applied to a sample 13 cm in length by 13 mm width and up to 13 mm in thickness for 10 s. It is withdrawn until the sample flame goes out, and then reapplied for 10 s. If sample flame duration in both cases is less than 5 s, and the sample does not drip flaming particles onto and igniting surgical cotton, the compound can be rated V-0. If, instead, the duration is 25 s, the compound is rated V-1. If surgical cotton beneath the sample ignites, the compound is rated V-2. The ASTM vertical flame test analog is D 3801.

In the UL-94 horizontal flame test, a 25 mm Bunsen burner flame is applied to a sample of the above dimensions clamped horizontally. Burn rate is measured in terms of flame spread per time. With specimens thicker than 0.12 in (3.1 mm), a burn rate of less than 1.5 in/min (38 mm/min) is considered to have passed and is rated 94HB. With thinner specimens, a burn rate of less than 3 in/min (76 mm/min) is acceptable. The ASTM horizontal flame test analog is D 635. If the sample is too flexible for effective use of D 3801 or D 635, provision is made in D 4804. An additional horizontal flame test for use with automotive interior components is described in ASTM D 5132 (comparable to Federal Motor Vehicle Safety Standard 302). An attempt to correlate more closely with the popular UL-94 procedures has resulted in ASTM E 2061.

Cone Calorimeter The cone calorimeter was developed by the National Institute for Standards and Technology (NIST), formerly the National Bureau of Standards (NBS). Adjustable heat input is provided by an electric coil shaped like a cone—hence the name. Heat release from combustion is determined by measurement of oxygen consumption, per ASTM D 1354. In addition, the equipment provides measurements of time to ignition and of smoke density. The use of the cone calorimeter is now the most prevalent method of estimating ease of ignition and contribution to combustion under a range of conditions. Since the equipment is expensive, it is often convenient to use the facilities of test laboratories, including UL. Even with the range of options offered by the cone calorimeter, it is often difficult to achieve correlation with larger scale test equipment.

Prior to the widespread acceptance of the cone calorimeter, use was made of the Heat Release Calorimeter developed at Ohio State University, per ASTM E 906. The level of heat flux is adjustable, but not as extensively as with the cone calorimeter. Heat release from combustion is recorded throughout the period of ignition. Smoke density is measured similarly to the cone calorimeter. ASTM E 1354 and E 906 data correlate at comparable levels of heat flux input.

Steiner Tunnel Per ASTM E 84, a 25 ft (7.6 m) tunnel is used to measure the burning characteristics (usually) of building materials. When used with wire and cable, the operating standard is UL-910 (also designated NFPA 262 by the National Fire Protection Association). The sample is ignited with a 1.4 m, 300,000 BTU (320 MJ) methane flame in a 240 ft/min (73 m/min) air draft for 20 minutes. Flame spread is observed through windows; smoke density is observed through attenuation of a beam of light in the exhaust and compared as a percentage of a red oak control taken as 100. Flame spread of less than 5 ft (1.5 m) beyond the original ignition zone is taken as an indication of a high degree of fire safety. It should be noted that it is possible to have fires in actual circumstances with far higher heat input than that above, particularly with combustion of petroleum products. The expense of construction and operation of a Steiner tunnel is such that tests are almost always carried out by consulting laboratories.

Smoke Generation As noted above, the cone calorimeter and Steiner tunnel also measure smoke generation. More commonly, the NBS Smoke Chamber is used, per ASTM E 662. A chamber measuring 36 in × 24 in × 36 in (0.9 m × 0.6 m × 0.9 m) is used. An electric furnace provides a heat flux of 2.5 W/cm^2 at the sample surface, and obscuration of a vertical light beam is determined photometrically, yielding an optical density. This is run while the sample is burning (flaming mode) and after extinction of the flame (nonflaming mode), the latter commonly yielding higher smoke density. It should be noted that smoke generation measurements should be used only to rank a series of samples. Results from one procedure should not be expected to correlate with data obtained by other methods.

Prior to the development of the NBS Smoke Chamber, the simpler Arapahoe Smoke Chamber was widely used, per ASTM D 4100. In this procedure, the smoke particles are collected in the stack on filter paper and weighed. This is very useful if the investigator is studying mechanisms of smoke generation and suppression and wishes to collect the particles to determine, for example, the extent of surface oxidation. It can be combined with analysis of the effluent gases so as to estimate the balance of carbon particles versus oxides of carbon. (A number of additives that reduce smoke generation operate by catalysis of carbon particle oxidation.) On the other hand, for simply characterizing the smoke generation of a given compound, the NBS Smoke Chamber is (with reason) more widely accepted. Data from the two methods typically show very marginal correlation.

Toxic and Corrosive Gas Evolution The simplest method to check for corrosive gas evolution (hydrogen chloride in the case of PVC) is to use the ISO procedure, IEC 754-2. In this method, the gases evolved from combustion of the product (typically a wire covering) in a tube furnace are swept into collecting tubes containing distilled water, and the drop in pH is measured. Using ASTM D 5485, the gases evolved from combustion in a cone calorimeter (in this case referred to as a cone corrosimeter) are swept into contact with a metal target, whose weight change is measured. Suitable targets, as well as special purpose apparatus for this test, are available from Rohrback Casasco. A number of testing laboratories also perform the D 5485 procedure.

A useful alternative for electrical components is given in ISO DIS 11907-3, in which the evolved gases contact a printed circuit board of standard design, and the extent of combustion needed to disrupt operation of the board is determined.

At the same chlorine content, CPE evolves considerably less hydrogen chloride during combustion tests. PVC/CPE combinations should be considered for applications requiring low corrosive gas evolution. The most common compounding technique is to use ultrafine calcium carbonate as filler for maximum hydrogen chloride absorption. This may be necessary in replacing lead stabilizers (whose reaction products with hydrogen chloride are typically very heat-stable) with zinc-based equivalents.

The most reasonable method of assessing the toxicity of gases given off during combustion is to determine analytically the concentrations of toxicants evolved under standard conditions and compare the results with known LD_{50} values. This is exactly the procedure sanctioned in ASTM E 1678. Unfortunately, regulatory authorities are often not satisfied with such conclusions, and require suppliers of various articles to establish the conditions under which laboratory animals are actually annihilated by combustion gases. The most notorious of these procedures is referred to as the University of Pittsburgh test. In this procedure, four mice are subjected to somewhat diluted combustion fumes under standard conditions for 30 minutes, followed by a 10-minute period of (possible) recovery. The quantity of compound burned is increased until there are only two murine survivors, the LC_{50} value being the quantity of test sample whose combustion is needed to kill two of four. Survivors as well as victims may then be subject to autopsy to determine cause of death and, in survivors, the extent of damage. The usual cause of death with combustion of PVC articles is carbon monoxide poisoning, as is the case with most polymers. LC_{50} values for PVC compounds are highly variable and marginally reproducible. With laboratory rats, whose susceptibility to toxic gases is thought to be much closer to that of humans, LC_{50} values are much higher than with mice. Nevertheless, the University of Pittsburgh protocol continues to insist on mice. It should be noted that this procedure has neither ASTM nor ISO sanction. Testing is carried out by UL and others. A less popular, similarly unsanctioned, alternative is the NBS Smoke Toxicity test. Again, the quantity of combusted product needed to kill animals is determined. It is difficult to understand why toxicity assessment cannot be limited to predictions arrived at using ASTM E 1678, conclusions from which have been accepted by fire safety authorities.

18.9 ELECTRICAL PROPERTIES

Volume Resistivity Volume resistivity (VR) is the resistance between two electrodes separated by a cube of unit volume; hence, it is measured in ohm cm^2/cm, or ohm cm. In a wire covering, it characterizes the resistance to loss of electrical energy by leakage through the insulation. Thus high values are desirable. If, on the other hand, the extruded layer is expected to be semiconducting, low values are desired. Pure PVC has very high VR, greater than 10^{15} ohm cm at 20 °C. Addition of polar ingredients, such as ester plasticizers, drop VR to $10^{10}-10^{15}$ ohm cm at 20 °C, depending on type and level. Measured values are highly temperature-dependent. An insulation with VR of 10^{14} ohm cm at 20 °C may drop to $10^{11}-10^{12}$ ohm cm at 50 °C. This trend is typical of ionic conduction, where increased molecular motion promotes leakage. A semiconductor with a VR of 10^3 ohm cm at room temperature will, contrarily, show a substantial increase at higher temperatures. This behavior is typical of electronic conduction, where increased molecular motion interferes with conduction. Thus, as temperature is increased, both insulations and semiconductors become less effective. The most reasonable solution—increasing the size of the conductor to limit heat buildup—is less attractive to manufacturers than imposing demands on formulators for wire coverings of greater stability but lower cost.

In the range of $10-10^{10}$ ohm cm, VR can be determined with reasonable precision using an ordinary ohmmeter, using the equation VR = measured resistance × area of the electrode/thickness of the sample. Above such limits, and for best precision, resistance is determined with a Wheatstone bridge per ASTM D 257. Here, the resistance of the sample is balanced against that of standards with a null galvanometer. Suitable equipment is supplied by General Radio and others, including cells for measurement of samples die-cut from molded sheet. Such samples are run after standard periods of conditioning (ASTM D 618) and after either heat aging or water immersion at 75 or 90 °C. Tests run after heat aging indicate that VR values are commonly sensitive to stabilizer consumption and the development of chlorinated reaction products. This is particularly useful in dark compounds where discoloration cannot be followed. It is a technique deserving of wider application.

VR values on sheet samples after hot water immersion may or may not correlate with tests run on wire samples. In the latter, what is measured is insulation resistance (IR), the ratio of the applied voltage to the total current between the conductor as one electrode, and the water bath as ground. It is expressed as megohms/1000 ft (305 m) of wire. What can be said is that compounds where sheet samples that perform very badly (IR drops to very low values or to zero) will certainly perform poorly on wire, but that compounds where sheet samples perform very well, may perform well when properly run on wire.

Surface resistivity is the leakage of current along the surface, expressed in ohms. It is also measured with a Wheatstone bridge and null detector, but with both electrodes on the same side of the sample. It is used to evaluate the effect of antistatic agents and suitability for service in charge dissipation.

Dielectric Strength Dielectric strength, the electrical potential per thickness at which a conductive path is formed, is useful for determining the presence of voids and other defects, such as points of poor dispersion, in wire insulation. The relevant ASTM specification is D 149. In production, insulated wire is run continuously through a high-voltage source, referred to as a "spark tester," the potential being applied through a series of dangling chains with the conductor grounded. Voids and points of egregiously bad dispersion will cause a discharge. The event is recorded, and often marking ink is sprayed on the failure point so as to facilitate removal or repair. With low-voltage constructions that are to be cabled and jacketed, and with some parallel cords, a limited number of spark failures are allowed, since the likelihood of nearby insulated conductors having failed at the same point is vanishingly small. Spark testing procedures are covered in ASTM D 4566.

Reels of insulated wire are commonly subjected to a dielectric strength test referred to as a "withstand," in which a potential several times greater than the service capacity is applied, often after the reel has stood for 24 hours in water at room temperature. In this procedure, also called a "tank test," the potential is applied to the conductor and the tank is grounded (the reverse of spark testing). This test also identifies uninsulated voids, and tends to discover points of bad dispersion near the conductor surface. The spark test procedure is more sensitive to poor dispersion near the outer surface of the insulation. Dielectric withstand procedures are covered in ASTM D 470.

On sheet samples, dielectric strength measurements can be used to spot poor dispersion, particularly of carbon black. The applied potential can be AC or DC, depending on anticipated service. With AC testing, frequency influences the values obtained. In both cases, the potential may be steadily increased until failure occurs (the "rapid rise" method). Alternatively, the potential may be increased in steps per UL and ASTM protocols. Rapid rise tests generally yield higher values of dielectric strength.

Dielectric Constant Dielectric constant, the ratio of capacitative charge created by a given potential in an insulator compared with that which would have resulted in a vacuum, is a basic material property related to polarizability. It is referred to in ASTM standards also as "relative permittivity," an analog of magnetic permittivity, and throughout the wire industry as specific inductive capacitance (SIC). Measurements of SIC and the related construct power factor (PF), the total loss of transmitted energy from leakage, inductive, and capacitative effects, are described in ASTM D 150. Measurements are made with a bridge that balances both capacitance and resistance against controls.

Compared with polyolefin wire coverings with SIC values as low as 2–2.5, PVC yields higher losses. Rigid PVC compounds are in the range of 3.2–3.6. Flexible PVC insulations have typical SIC values of 4.5–6.0, the lowest values being consistent with use of calcined clay filler, and the highest with aromatic ester plasticizers. In power transmission applications, such as building wire, low SIC and PF are desirable so as to minimize energy loss, which adds to expense, and resultant heat buildup, which decreases service life. In communications wire, low values are important so as to maximize the extent of information that can be carried. The modulations that carry data are not limited to the conductor (as in pouring water down a pipe) but exist also in the insulation. The signal strength of such modulations is negatively affected by high SIC.

Formulating for low SIC and PF commonly involves choice of ester plasticizers having substantial aliphatic hydrocarbon side chains, use of hydrocarbon secondary plasticizers, use of calcined clay filler, reduction generally of polar additives, and (unfortunately) use of lead-based stabilizers.

18.10 PLASTISOL TEST METHODS

Air Release Plastisols and, to a lesser extent, organosols often contain considerable air from mixing that must be removed prior to processing or testing of finished properties. The solvent content of organosols tends to promote air release on standing. Plastisol viscosity depressants, typically hydrocarbons or aliphatic carboxylic acids, also promote air release, but are generally unsuitable for low-fogging (see in the foregoing) applications. The most popular air release agents, oleic and tall oil acids, are fog contributors, but remain in wide use in nonautomotive uses. Proprietary air release additives include polyglycol derivatives (e.g., Byk Chemie GP-3155) and silicones (e.g., GP-3160). The latter are low-fogging, but generally interfere with adhesion.

Prior to fusion for determination of physical properties in the laboratory, plastisol samples or laboratory batches are de-aerated using a vacuum desiccator. The rise in height of the plastisol before air release is sometimes taken as an indication of the resistance to air release. In other ad hoc methods, an air bubble of specific volume is injected with a syringe below the surface and the time required for it to break is measured. It is just as convenient and more meaningful to measure the decrease in volume or observe the evolution of air on addition of controlled amounts of air release agents. In practice, physical properties of the fused compound are determined versus level of air release agent to arrive at a useful formulation.

Viscosity As plastisols are typically non-Newtonian, it is often useful to measure viscosity at more than one shear rate. A given plastisol, for example, may require low viscosity at high shear rates for application with a spray gun or high-speed coater, but, once applied, may need high viscosity at low shear rates to prevent sag or excessive penetration into a backing. Viscosity at low shear rates is most often measured by determining the back-torque on a rotating cylinder using a Brookfield® viscometer per ASTM D 1824. Brookfield viscosities useful in a given process are determined empirically and through experience.

Viscosity at high shear rates comparable to those in many processes are often measured using the Severs® extrusion rheometer (e.g., Burrell Corp. Model A-120) per ASTM D 1823. In this method, the plastisol is forced through a standard orifice under (preferably) nitrogen pressure. The weight of plastisol extruded versus time is determined at a series of applied pressure settings. The radius of the orifice, the length of the capillary, the density of the plastisol, and the weight per time extruded are used to calculate shear stress and shear rate, a geometrical factor being applied to the ratio to obtain the viscosity in poise. The same results may be obtained with other types of capillary rheometer. Again, the relation to actual processing depends on experience and empirical correlation.

Viscosity is often controlled by additives. The level of the chosen plasticizer appropriate to fused physical properties often yields a viscosity found too high in processing. Process viscosity is then lowered by addition of low levels of mixtures of hydrocarbons (e.g., Viscobyk® 4040, Byk Chemie) or aliphatic acids (e.g., Viscobyk® 5050). Both volatilize during fusion. Generally, such additives are not suitable for low-fogging applications. When high thixotropy is needed in order to provide suitable processing viscosity, but low viscosity at low shear, urea-based additives such as Byk® 410 thixotropic control agent are added.

Gelation and Fusion En route to fusion, the plastisol passes through a gel state. Gelation is the point where all of the liquids have been absorbed, forming a soft solid. Gelation rate is important in applications where this state, dependent on time and temperature, determines the thickness of product. A common method is to run Brookfield® viscosity versus time in a heated oil bath, for example at 100 °C. Viscosity is plotted as a function of time, reaching a plateau on gelation.

The complete path of gelation, fusion, and melt behavior is often determined using a torque rheometer. The latter can be set to a program of temperature increase to processing conditions, following a rate thought appropriate to the process. This can be extended to provide a measure of heat stability as well. The use of this method has been increasing.

In cases where viscosity–temperature behavior is of less concern, the plastisol can be coated on a glass or stainless steel sheet to the desired thickness using a wire-wound bar, or onto backing or release liner by means of a laboratory coater. Samples are then placed in a circulating air oven at, for example, 190 °C for various time periods. Physical property measurements are then used to determine fusion time. Additional exposure can be used to measure static heat stability. Such measurements can also be carried out with the Metrastat® apparatus.

18.11 ANALYSIS OF PVC COMPOSITIONS

PVC compositions are typically analyzed as an indication of correct formulation or to deconstruct competitive compounds. Occasionally, analysis is required by specification, such as the level (usually zero detectable) of vinyl chloride monomer (VCM). The latter is carried out by headspace gas chromatography (GC) per ASTM D 3749 for resins, and ASTM D 4443 for compounds. Such analyses are routinely done by suppliers. The formulator in the field will usually send samples to a testing laboratory. This is also the case with trace analysis, often for levels of lead, cadmium, arsenic, or mercury.

Surface analyses, such as with X-ray photoelectron spectroscopy (XPS = ESCA), scanning electron microscopy (SEM), and dispersive X-ray analysis (EDX, WDX) are discussed in Section 17.7 because they are used routinely in characterizing vinyl composites. They are also useful in other connections, such as changes to vinyl surfaces from weathering or exposure to aggressive media. Fourier transform infrared (FTIR) analysis is also discussed in Section 17.7.

Specific Gravity Specific gravity (SpG), the ratio of the density of the compound to that of water at a given temperature (4, 20, or 25 °C) is usually measured per ASTM D 792. In Method A, a sample is weighed in air and in pure de-aerated water. This can be done directly using a gravitometer (e.g., the Fisher Scientific Gravitometer), which provides a direct reading of SpG. The method applies to single solid pieces. It can be used, versus control samples, to estimate the porosity in a dense sample or to determine the density of foamed samples. If a number of samples are run routinely, it may be preferable to set up a density gradient column. A density gradient is set up in a clear liquid mixture, and the depth to which a sample sinks is measured. The procedure is given in ASTM D 1505 (ISO 1183-2).

Method B of ASTM D 792 uses a gas pycnometer to measure the volume of a powder or a granulated or irregular solid. The displacement of gas, usually helium, from a vessel of known volume is measured by sensitive differential pressure indicators. Suitable laboratory equipment is manufactured by Quantochrome (UltraFoam® Pycnometer), Micromeritics (Accu Pyc® 1330), and others. This is also a convenient route to foam density. In troubleshooting production problems, SpG should always be checked, because of its sensitivity to misformulation.

Compositional Analysis Although common errors in compounding usually result in an aberrant SpG, some, such as use of a similar but nonidentical plasticizer, may not. In diagnosis of such problems, it is useful to proceed to more definitive tests. This involves separation of components. Treating the sample with an excess of warm tetrahydrofuran (THF) (typically 1–2 g compound in 50 ml) will dissolve the resin and most organic additives; fillers and pigments may then be centrifuged or filtered. These may be examined microscopically or quantitatively determined, versus controls, typically by an analytical laboratory. The THF extract can be dried and its infrared spectrum compared with control samples. Quantitative procedures are given in ASTM E 168; FTIR methods in F 1374. Addition of excess methanol will cause the resin to precipitate. This can be re-dissolved in THF, and the molecular weight distribution determined by gel permeation chromatography (GPC) along the lines of ASTM D 5296 (originally for polystyrene samples). Control samples must be used; the molecular weight distribution will be altered by mixing and processing. In general, the distribution will be more useful to the formulator than the average molecular weight, the quantity involved in dilute solution viscosity. In the absence of GPC, intrinsic or inherent viscosity may be determined on the resin via ASTM D 1243, or directly on known compounds per D 3591. General considerations pertaining to dilute solution viscosity measurements are given in D 2857.

Copolymers and PVC blends can be analyzed by quantitative carbon-13 nuclear magnetic resonance (NMR). The relative abundance of $—CH_2—$, $—CH—$, $—CH{=}CH—$, and $C—O—$ can be estimated closely. Blends with NBR can be assessed by prevalence of $—CN$ carbon. NBR and urethane blends should also be subject to proton NMR, quantifying $N—H$ as well as the various $C—H$ protons by chemical shift. With so-called "magic angle spinning" techniques, solid samples as well as solutions can be analyzed. NMR techniques are described in ASTM E 386.

The THF/methanol extract can then be pursued for organic additives by FTIR and GC/MS (ASTM D 4128) methods. Control samples are essential. It is likely that degradation products as well as original additives will be found; the pattern of such discovery is vital for the assessment of problems by the formulator. Infrared analysis of PVC compounds by infrared methods is covered in ASTM D 2124. Direct qualitative determination of monomeric plasticizers requires brief extraction with acetone followed by GC identification; this method is found in ASTM E 355.

Moisture content has been classically determined by Karl Fischer titration using semi-automated apparatus as described in ASTM E 203. This has been largely replaced in routine operations by weight loss determination using automated balances, often with microwave heat input (see Volatile Loss in the foregoing). Such operations are covered in ASTM D 6980. With suitable columns and detectors, GC methods can be used, particularly in combination with TGA loss of water. Proton NMR is also sensitive and can distinguish between water of hydration and physically adsorbed moisture.

18.12 LABORATORY SOFTWARE

A laboratory information management system (LIMS) comprises computer software used for the management of samples, instruments, standards, and functions such as work flow and time, accounting for a number of users. It enables maintaining the process of information gathering, decision making with regard to experimental direction, calculation, review, and dissemination of findings within the technical department. The goal is to create an environment where:

- Instruments used are integrated into the network; receive instructions and work priority from LIMS; and return raw data and finished results to a central repository.
- Personnel perform calculations, update documentation, and review results from connected instruments, and reference databases using electronic laboratory notebooks.
- Management reviews such progress and confers with technologists, insuring rapid recognition of unusual or unexpected events, often the source of innovation.
- Participants from other departments, such as sales and marketing, enter R&D requests and review progress.

LIMS is primarily concerned with maximizing the effect of R&D investment, adjusting goals as research proceeds, and providing early recognition of potential breakthroughs. It is basically a communication mechanism. Useful software includes Perkin Elmer Labworks®, particularly in connection with their analytical equipment; Adept Scientific's LIMS, which interfaces with their ChemDraw® and ChemOffice® programs; and Agilent LIMS, particularly with chromatographic equipment. Outdated LIMS may be updated with software from Starline Corp. Instruments that can interface automatically with LIMS are said to be systems and supervisory control and data acquisition (SCADA) enabled.

The optimization of R&D in regard to achievement of objectives and control of investment is known as high-throughput experimentation (HTE). Its steps are as follows:

- Design: set objectives, select R&D team, propose methodology →
- Preparation: procure/prepare samples for evaluation →
- Measurement: samples tested per design of experiment →
- Modeling: validation of testing; conclusions → Design

The HTE cycle aims to enable a considerable number of experiments in as short a period of time as possible by emphasizing design, running experiments in parallel aided by miniaturization, maximizing use of automatic capability, and developing maximum feedback. Programs for implementing HTE are available from, among others, Tessella Supply Services LLC.

Software for data analysis, integration, and manipulation are available from, among others, SAS and Spotfire.

CHAPTER 19

Regulatory and Legislative Matters Affecting the Plastics Industry: Health, Safety, and the Environment

LEWIS B. WEISFELD

19.1 WHAT IS A LAW, WHAT IS A REGULATION?

In the United States, Federal "Acts" originate in Congress. After agreement by a House–Senate conference committee, the Act is passed on to the President for signature (or veto). Once signed into Public Law, it is then assigned to the appropriate government regulatory agency, which is charged with drafting the rules under the Act

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and enforcing them. There are more than 30 Federal departments and agencies that have significant regulatory responsibility for interpreting and enforcing public law. Those public laws within the health, safety, and environmental scope of this text include:

- The Federal Food, Drug, and Cosmetics Act (FFD&CA)[1,2]
- The Toxic Substance Control Act (TSCA)[3]
- The Resource Conservation and Recovery Act (RCRA)[4]
- The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or "Superfund") and the Superfund Amendments and Reauthorization Act (SARA)[5]
- The Clean Air Act (CAA)[6]
- The Clean Water Act (CWA)[7]
- The Safe Drinking Water Act (SDWA)
- The Occupational Safety and Health Act (OSHA)[8]
- The Consumer Product Safety Act (CPSA)[9]

The Federal Agencies charged with the administration of Public Laws will issue regulations. First, an *Advance Notice of Proposed Rulemaking* (ANPRM) will appear in the *Federal Register* (FR), a daily publication. This consists of a first attempt to formulate the regulation. Public meetings and a comment period will also be announced in the *Federal Register*, and this will lead to publication of a *Notice of Proposed Rulemaking* (NPRM) and possibly more public meetings and comment periods. Eventually, the *Final Rule* will appear in the *Federal Register*, and upon its publication it becomes the law of the land on the date specified. Once a year, these rules will be republished or codified in the *Code of Federal Regulations* (CFR) and the *United States Code* (USC).

19.2 FEDERAL AGENCIES

19.2.1 Food and Drug Administration

The principal interest of plastics industry in the *Federal Food, Drug and Cosmetics Act* (FFD&CA) is in the area of plastics food and beverage packaging and plastics medical devices. The Federal Food and Drug Administration (FDA) administers these regulations. Under the provisions of the 1938 FFD&CA, no premarket clearance was required for any type of food packaging. If a packaging material rendered the food unfit for human consumption, the only recourse FDA had was to move against the product itself by seizure and prohibition. Food processors and packagers, alike, required reasonable assurances that the food container or processing equipment used would pose no public health problems, and that the packaging material would not adulterate the food contained. Some sort of indemnification was sought from the packaging supplier, and an opinion or "letter sanction" solicited from the FDA and/or the U.S. Department of Agriculture was usually sufficient.

The 1958 Food Additive Amendments changed this procedure, and the FDA was given the authority to regulate packaging materials and food processing equipment, the same way as substances deliberately added to food, that is, to regulate *indirect food additives*. The current rules are codified in Title 21, *Code of Federal Regulations (21CFR).* Under present law, any substance that comes in contact with food is considered unsafe unless it is used in conformity with a regulation issued by the FDA. This includes not only the base polymer, but also residual monomers, catalysts, and compounding adjuvants (e.g., heat stabilizers, antioxidants, lubricants, pigments, and fillers) that can reasonably be expected to migrate from the packaging media and become part of the packaged food. The use of certain of these substances is permitted if they are *generally recognized as safe* (GRAS), were *prior sanctioned* by the FDA or USDA before 1958, or are not reasonably expected to become a component of the food under the intended conditions of use. Also, the quantity of the indirect food additive must not exceed the amount that is reasonably required to achieve the intended technical effect in the food-contact article.

A large number of necessary processing and property adjuvants or indirect food additives are considered safe for use in the fabrication of plastics food-contact articles, and these are found in Title 21, *Code of Federal Regulations (21CFR).* Some of these are:

21 CFR Section §177, subpart B	Substances used as a component of single and repeated use food-contact surfaces
§ 178	Adjuvants, production aids, and sanitizers
§ 178.2010	Antioxidants and/or stabilizers for polymers
§178.2650	Octyltin stabilizers in vinyl chloride plastics
§178.3740	Plasticizers in polymeric substances

Di(2-ethylhexyl) adipate (DOA), the most widely used plasticizer in flexible PVC meat and produce wrap, is listed under §178.3740, but di(2-ethylhexyl) phthalate (DOP or DEHP) is not. DOP is prior sanctioned (i.e., before 1958) for foods of high water content. Both DOA and DOP have been under regulatory scrutiny since they were found to be carcinogenic in animal feeding tests.[10,11]

If the producer of food packaging materials can trace the packaging ingredients of an intended formulation through 21CFR, it is sufficient to stipulate to the client that *this material is considered safe for use in food-contact applications according to the provisions of Title 21, Code of Federal Regulations* and even cite the appropriate provisions, if that information is not proprietary. No material or ingredient is specifically "approved," since the FDA does not approve anything. Liability rests entirely upon the material supplier. If no provision exists for any specific polymer or adjuvant, the producer must then petition the FDA to amend Title 21 to provide for such usage. The *Food Additive Petition* (FAP) then becomes a matter of public record (i.e., published in the *Federal Register*) and must include all the necessary information to allow the FDA to make a determination on safety under the intended condition of the product's use.

The FAP is drafted in the form prescribed in 21CFR §171.1. It encompasses probable consumption of the food product, the cumulative effect of the additive on human diet, animal feeding tests and extraction or migration data. In addition, it may include an evaluation under the *Delaney Clause* portion of the 1958 Amendment that instructs the FDA to ban any food additive that can cause cancer in man or any species of animal, regardless of the amount of substance involved or actual human cancer risk under the conditions of use. Finally, it must contain an *Environmental Impact Assessment Report* (EIAR) considering such things as the management of new waste material sources, economic impact, and risk–benefit analysis. Since the EIAR must of necessity contain proprietary marketing information, the FDA will treat parts of the FAP as *Confidential Business Information* (CBI) upon specific request. Guidelines for the extraction and safety data required in a Food Additive Petition will change over time. It is always best to seek the opinion of the FDA before embarking on the time and expense of an FAP.

Liquor packaging presents an additional problem in that containers for distilled spirits must be approved by the Bureau of Alcohol, Tobacco, and Firearms (BATF, under the Treasury Department), as well as being provided for in 21CFR. BATF for a long time did not condone the use of rigid polyvinyl chloride bottles for such, because of the vinyl chloride monomer (VCM) situation of over a decade ago. However, polyethylene terephthalate liquor bottles now abound.

Recently, the FDA has established a new policy that sharply abridges the Food Additive Petition process. Where the likelihood or extent of migration of a substance to food is so trivial as to not require regulation of the material as a food additive, information about the proposed use of the additive will undergo an abbreviated review by FDA as opposed to the former extensive review and formal issuance of a new regulation. Of consideration in formulating this rule was *Monsanto v. Kennedy, 613 F2nd 947 (D.C. Circuit 1979)*, wherein Monsanto argued that there is no migration of acrylonitrile copolymer resulting from use of their beverage bottles. The agency now holds that the "threshold of regulation" be set at 0.5 parts per billion anticipated dietary intake per day, which is 2000 time lower than the no-effect level of the vast majority of indirect food additives it has examined.[12]

Drug and biologics packaging and the use of plastics in medical applications (i.e., "devices") also fall under the purview of the FDA. Because of its long history of safe usage and its wide range of desirable physical properties, from flexible to rigid, polyvinyl chloride and its copolymers enjoy a paramount position in medical packaging and application. This market is under concerted attack by environmental activists and is, as a consequence, slowly being eroded by alternative materials such as thermoplastic elastomers. Although drug and biologic (e.g., containers for blood, plasma, and intravenous solutions) packaging materials may initially be selected from those food-contact substances included in 21CFR, this is usually not sufficient. The FDA has published guidelines for such packaging. Proposed packaging for these applications is usually petitioned as part of the *New Drug Application* (NDA) along with the drug or biologic to be considered, or as part of an FDA petition on the new medical device. The relevant test procedures are described in the *United States Pharmacopoeia* (USP).[13] This often involves animal implantation and extraction tests with progressively aggressive solutions, followed by injection of these extracts into the test animals. The least stringent is USP Class I, up to Class IV. Class III devices are those that support or sustain human life, are of substantial importance in preventing impairment of human health, or present a potential unreasonable risk of illness or injury. These require a pre-market approval (PMA) application, the most stringent type of device marketing application required by FDA. If the device is "substantially equivalent" to a previous approved one or if not designated Class III, a pre-market notification submission, referred to as a "501(k)," is sufficient.

Medical device manufacturers had long complained of excessive delays in the review process. The FDA Modernization Act of 1997 expanded the humanitarian device exemption (HDE) and allowed greater patient access to devices in the investigational stage and loosened the strictures of the PMA process. With the passage of the Medical Device User Fee and Modernization Act (MDUFMA) in October 2002 (www.fda.gov/cdrh/mdufma/), the FDA was authorized to assess fees for pre-market reviews of medical devices, with the intention of building the necessary infrastructure to expedite reviews and aiding the manufacturer. Small businesses (those with annual sales/receipts of less than $30 million), pay lower fees than larger companies. Extra relief was added in that third-party assessments may now be performed. These fees apply to any PMA, pre-market report, supplement, or 501(k) submitted after October 2002. Fees are to be adjusted each year to account for inflation, changes in the FDA's workloads and other factors.[14]

19.2.2 Environmental Protection Agency

The Environmental Protection Agency (EPA) is the largest Federal agency regulating health, safety and the environment (HSE), and it deals with more acts than any other. Under its purview, we find the Toxic Substance Control Act (TSCA), the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund") and the Superfund Amendments and Reauthorization Act (SARA), the Clean Air Act, the Clean Water Act, and the Safe Drinking Water Act, all of which are of interest to the plastics industry. Since its formation in the early 1970s, this agency has issued more regulations affecting the plastics industry in the HSE area than any other Federal department or agency, and continues to do so. The EPA Administrator may soon become a member of the President's Cabinet, and the agency would change its name to the "Department of Environmental Protection."

Toxic Substance Control Act (TSCA) The TSCA was signed into law in October 1976 and became effective on January 1, 1977. It gave the EPA the authority to deal with toxic problems after they occurred and established a new approach to identifying and avoiding problems before they arose. The four major functions of the TSCA are information gathering, regulation, pre-manufacturing requirements, and coordination of the various other regulatory agencies to control health and environmental hazards through dissemination of data derived from the Act, research, data systems and other means.

Early on, the EPA established an Inventory List of known industrial chemicals that were manufactured before implementation of the TSCA. This is not the same as the FDA's list of Title 21 "sanctioned" food-contact chemicals, but each substance is subject to hazard review. The chemical manufacturer, importer, or processor should note that Sections 4 and 8 of the TSCA enable the EPA administrator to call for unpublished data on important health and environmental aspects of potentially harmful substances through testing, record keeping, and reporting. If the administrator finds that a substance may present an unreasonable risk or that data on which to base an assessment is lacking, testing may be necessary and the costs will be borne by the manufacturer or processor. Proposed and (mandatory) final *Preliminary Assessment Information Rules* (PAIRs) *and Comprehensive Assessment Information Rules* (CAIRs) are published periodically in the *Federal Register*, requiring manufacturers, importers, and processors to submit information (e.g., production and use volumes, potential exposure, and environmental releases) on various chemicals, many of which go into plastics as monomers or adjuvants.

Even if a substance is on the Inventory List, the EPA can issue a *Significant New Use Rule* (SNUR) for it when the agency deems that the material may pose a hazard to either human health or the environment. Under an SNUR, a manufacturer or processor may be required to submit notice to the EPA for review at least 90 days prior to manufacture or use.

If the chemical in question is not on the Inventory List, then a *Pre-Manufacturing Notice* (PMN) must be submitted at least 90 days before commencement of manufacture (TSCA Section 5(a)(1)). PMNs are published in the *Federal Register*, allowing a time period for anyone with adverse data to comment. These PMN notices are usually purged of Confidential Business information (CBI), sometimes omitting even the name of the petitioner. Essentially equivalent to a PMN is the *Test Marketing Exemption* (TME) for new chemical entities.

EPA receives over 2000 PMNs each year. EPA says that it expects this number to fall by one-third under the relatively new *Polymer PMN Exemption Rule*, which became effective on May 30, 1995.[15] Under this 1995 rule, the agency promulgated amendments to expand the exemption criteria and exempt manufacturers of eligible polymers from certain Section 5 pre-manufacturing notification requirements. The agency has determined that the manufacturing, processing and distribution in commerce, use, and disposal of new chemical substances meeting the revised polymer exemption criteria will not present an unreasonable risk of injury to human health or environment under the terms of the exemption. These final amendments reflect criteria developed and used by the EPA to assess the hazards associated with new polymeric substance over the past 20 years that the new chemical program has been in place. The agency believes that these amendments will encourage the manufacture of safer polymers by reducing industry's reporting burden for this category of chemical substances. In effect, the rule frees many categories of polymers from PMN requirements and cuts the time for placing many new polymers on the market.

In addition, the EPA has granted exemptions for small quantity manufacturers and importers under TSCA Section 5(h)(4) for persons who manufacture certain chemical substances in quantities of 10,000 kg or less per year.[16] Also, the amendment adds a new Section 5(h)(4) exemption category for certain chemical substances with low environmental releases and human exposure. This became effective on May 30, 1995, as well.

Resource Conservation and Recovery Act (RCRA) RCRA was signed into law in 1976 and currently regulates the management of hazardous waste. Undoubtedly, it was intended to do more, and Congressional reauthorization contains language reflecting on the disposal and recycling of nonhazardous municipal solid waste such as plastics packaging and other plastics items. RCRA rules are found in Title 40, *Code of Federal Regulations*. Within RCRA and under Congressional mandate, EPA has more recently completed an extensive list of landfill restrictions and prohibitions.

Wastes that are identified as hazardous come within the scope of RCRA's "cradle-to-grave" management program, from point of generation to final disposal. RCRA regulations establish standards for hazardous waste treatment, storage and disposal facilities allowed to receive such wastes; even wastes not identified as hazardous must still comply with Subtitle D of RCRA. Generators of hazardous waste are required to determine whether or not they have a listed hazardous waste; obtain an EPA identification number from the administrator before treating, storing, transporting, or disposing of the hazardous waste; maintain manifests and comply with pretreatment regulations; and submit annual reports. They must obtain an EPA permit either from the EPA itself or from the state in which they operate, provided that state has an EPA-approved hazardous waste program. Some relief and exclusions are permitted small businesses and others under specific conditions and petitions.

For the incineration of hazardous waste, three performance standards have been set: Organic wastes must be destroyed with an efficiency of 99.99 percent; gaseous hydrogen chloride (e.g., from the incineration of PVC scrap) must be reduced 99 percent or to less than 4 lbs per hour, and particulate matter emissions may not exceed 180 mg per dry cubic meter of stack gas. The EPA requires test burns on all incinerators to ensure that these conditions are met, a major expense costing companies up to $100,000 for each unit.

Superfund (CERCLA) The two important laws under the label of "Superfund" are the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* (CERCLA) and the *Superfund Amendments and Reauthorization Act* (SARA). Whereas RCRA is designed to prevent future environmental contamination, Superfund provides a means to clean up existing hazardous waste sites and to rectify future accidental spills of hazardous substances.

The major provision of CERCLA is the establishment of two multibillion dollar trust funds for this purpose, and most of this money comes from a tax on a large list of chemicals designated as hazardous to either health or environment. The major impact of Superfund on plastics processors is expense. For example, the tax paid by users of ethylene, about 1 percent of the list price, in the manufacture of polyethylene resins will be passed on from the resin maker to the compounder, and so on. Owners and operators of hazardous waste storage, treatment, and disposal facilities contribute to these trusts as well.

Hazardous waste sites eligible for Superfund cleanup money are those listed in the EPA-determined National Priority List, which seems to grow every month. Superfund does not release those responsible for the pollution from liability, nor does it give the government unlimited authority to spend money. In addition to the legal liability for reimbursing the government for cleanup costs, responsible parties may be liable for punitive damages if they resist government cleanup orders. Theoretically, at least, Superfund monies should never be exhausted. However, budgetary problems plague the program.

In October 1986, *SARA* was signed into law. In addition to establishing a new five-year program based on a $9 billion Superfund, SARA contains Title III, the *Emergency Planning and Community Right-to-know Act* (EPCRA). This requires manufacturers and processors of a broad list of hazardous substances (Title III, Sections 311, 312, and 313) to disclose their inventories, with material safety data sheets, and accidental releases to state and municipal emergency planning agencies, including their local fire departments. Final reporting thresholds were recently promulgated: 10,000 lb for normally hazardous substances, and 500 lb or the "Threshold Planning Quantities" for extremely hazardous chemicals.

Initially, common phthalate plasticizers were included in the "extremely hazardous substances" list (Section 311) of Title III SARA, but this has since been corrected. But many usual plastics compounding ingredients still remain listed and must be reported. For example, EPA denied a petition from a vinyl stabilizer company to de-list antimony tris(isooctylmercaptoacetate), a well known PVC stabilizer, since it considers the oxide decomposition products to be possible carcinogens.

Clean Air Act Dating back originally to 1955, the Clean Air Act vests the EPA with authority to regulate air emissions in two main areas: automobiles and new industrial plants. For industry, the agency mandates accelerated development of anti-pollution technology. Although the EPA does not, in itself, monitor emissions and regulatory compliance, it empowers the states to develop State Implementation Plans (SIPs), which it approves if they are in compliance with the National Ambient Air Quality Standards. EPA also issues Control Technology Guidelines to assist the states in determining reasonably available control technology for limiting volatile organic chemical (VOC) emissions from chemical and plastics plants. Some regulations of specific interest to the vinyl processor are vinyl chloride emission standards and test methods for measuring such emissions and similar final rules for flexible vinyl coating and printing operations. Current rules on air quality standards are found in Title 40, *Code of Federal Regulations*. The Clean Air Act was reauthorized by Congress in late 1990, and includes much more stringent pollution control regulations as well as time schedules for the phase-out of the stratospheric ozone-depleting chlorofluorocarbons and other chlorine-containing compounds.

Ozone and Particulate Matter EPA has been a court-ordered mandate to regulate even the tiniest particulate matter found in soot and smoke. Although the agency already regulates particles around 10 μm or less in diameter (PM_{10}), a debate rages over the health risks of even smaller particles. A six-city study of over 8000 patients by Harvard researchers in the early 1990s found a higher death rate in dirtier cities and suggested a link between the smaller particles and up to 60,000 premature deaths each year. The new $PM_{2.5}$ rule could require industry to spend billions of dollars for equipment to reduce 2.5 μm particulate matter from sources such as refineries and diesel-fueled vehicles.[17]

The agency began paying close attention to fine particulates in urban air over a decade ago, when the Harvard study in cities such as Steubenville, Provo, and Philadelphia showed that hospital visits for asthma and other respiratory illnesses rose and fell with the levels of these particles. On a smoggy day in Los Angeles, up to 20 percent of the mass of particulate matter less than 2.5 μm in diameter can come from hydrocarbons in evaporated or burned gasoline.

As a result of a court order, the EPA Administrator proposed sweeping changes to the *National Ambient Air Quality Standards* (NAAQS) that could force more than 100 cities to find costly new ways to control smog and also cause Americans to make significant lifestyle changes.[18] The agency acknowledged it could cost cities and counties nationwide a total of \$6.5–8.5 billion per year to make changes to meet the air standards. The decision was a blow to industry, which mounted a massive lobbying campaign against the proposal. Using state governors, mayors, and industry executives, the Air Quality Standards Coalition argued that the scientific evidence was sketchy and the economic impact too burdensome. The new standards would require communities to cut ozone levels by one-third to 0.8 parts per million (ppm) cubic feet of air from the current standard of 0.12 ppm.

The 1993 epidemiological study upon which the EPA's new particulate matter proposal is based is raising considerable controversy. The Harvard scientists who performed the study refuse to release the raw data (e.g., patient information and records) on the grounds that the breach of confidence would jeopardize future studies. Even the EPA does not have this data, and has joined the chorus demanding it. Finally, Harvard University offered a compromise on data release: they would allow analysis of these data by the Health Effects Institute, a well-respected Cambridge, Massachusetts, research concern with funding from both industry and government, provided the reviewers have ties to neither environmental groups nor the industries that oppose the proposal.[19]

EPA, however, remained adamant about the new clean air rules, despite objections coming from other agencies and even the White House staff of economic advisors, according to government documents released by the Air Quality Standards Coalition. Senior officials in the Treasury Department, Commerce Department, Transportation Department, and the Small Business Administration have argued in these documents that the tough new proposed standards for ozone and particulate matter are unjustified from both a medical and economic point of view. This disclosure followed a charge in Congress that EPA suppressed concerns with the Office of Management and Budget (OMB) about the economic impact of the proposed standards. In another development, the EPA admitted that it had overestimated the number of premature deaths that could be prevented as a result of the new rules. Initially, the agency claimed that 20,000 premature deaths could be prevented; now it says 15,000 deaths.

Clean Water Act Under the Clean Water Act, the EPA is required to adhere to a strict schedule in promulgating regulations for a large list of priority pollutants in water. Strict performance standards, pretreatment standards and effluent limitation guidelines now exist to control the discharge of pollutants into municipal sewers or publicly owned water treatment works (POTWs), into rivers, lakes, oceans and other bodies of water.

Under the related Safe Drinking Water Act, maximum contaminant level goals (MCLGs) have been articulated for a wide range of priority pollutants, including the PVC plasticizers di(2-ethylhexyl) phthalate and di(2-ethylhexyl) adipate. National Primary Drinking Water Regulations were promulgated in January 1991,[20] establishing Maximum Contaminant Level Goals (MCLGs) and current levels (MCLs) for 26 organic chemicals and 7 inorganic chemicals, including treatment techniques, monitoring, reporting, and public notification requirements. Best Available Technology (BAT) use is specified. In addition, regulations were proposed for a large number of volatile organic chemicals (VOCs), pesticides and barium compounds.[21] At the same time, EPA also issued new regulations on administrative enforcement policies.[22]

Clean Water Act reauthorization brings with it a new threat to the PVC industry. Claiming that PVC may be the world's largest source of the toxic dioxins, Greenpeace International, very active in Europe, has brought its battle to these shores. The activist group contends that PVC is the largest single user of chlorine-based feedstocks so that it must therefore be banned if success is to be realized in eliminating dioxins. According to Greenpeace, there are no uses of chlorine that they regard as safe. This message is being echoed by many associated local environmental activist groups.

Furthermore, the International Joint Commission (IJC)—a treaty organization established by the United States and Canada for the sound management of the Great Lakes region—has recommended the elimination of all chlorine-based industry in the area. In its Seventh Biennial Report, the IJC called for a new way of thinking by government, industry, and others about persistent toxic substances, those not easily destroyed by the environment. In this same report, the IJC rejected industry's call to temper its recommendations that chlorine and chlorine-based organic chemicals be phased out as industrial feedstocks. The commission says socio-economic considerations should, however, be taken into account. The commission also stresses that recent research shows that bioaccumulative toxins can disrupt hormone and reproductive systems and interfere with fetal development.

Although the IJC's recommendations had been initially eschewed by the U.S. Administration, the EPA has proposed, in its recommendations to Congress for a Clean Water Act reauthorization bill, a plan for reducing or prohibiting the discharge of chlorine or chlorinated products into bodies of water. Essentially, the use of chlorine compounds would be restricted or banned. A task force, to be convened within six months of the passage of the reauthorization bill, would examine the health effects of chlorine and organic chlorine products on humans and wildlife. After reviewing the task force's study, the EPA Administrator would be required to consider any number of "appropriate actions" within 30 months of the bill's passage. Environmental activist groups say the chlorine provisions do not go far enough, but the American Chemistry Council is "outraged" by them. Although the EPA Administrator had reassured industry that the agency has "no plan as part of the Clean Water Act proposal for a blanket ban on chlorine," the EPA is sticking to its resolve to begin examining use of the halogen and its compounds with the goal of eventually reducing, prohibiting, or developing substitutes for the chemicals.

As industry and environmentalists traded shots on the chlorine restriction proposals, the Senate Environment and Public Works Committee approved revisions to the 1972 Clean Water Act, clearing the way for a floor vote. The legislation would loosen certain water cleanup requirement for local governments, increase Federal loans to improve sewage treatment, and increase Federal regulation of non-point-source runoffs such as fertilizers and pesticides that wash from farmlands into lakes and streams. The revisions were supported by the U.S. Administration, but they do not include an EPA proposal to develop a plan to reduce or prohibit discharge of chlorine or chlorinated compounds into water. The bill would authorize $2.5 billion for a fund for sewage treatment in 1997.

19.2.3 Occupational Safety and Health Administration

The *Occupational Safety and Health Act* (OSHA) was enacted to assure safe and healthful working conditions for every working man and woman in the nation by authorizing enforcement of standards developed under the act; by assisting and encouraging the states in their efforts to assure safe and healthful working conditions; by providing research, information, education, and training; and for other related purposes. Part of the Department of Labor, OSHA is vested with the responsibility of setting occupational safety and chemical exposure standards, inspecting plants and issuing citations. Its regulations are found in Title 29 of the Code of Federal Regulations. An omnibus "air contaminants rule" was proposed in 1989 wherein OSHA confirmed its preference for engineering controls over respirator use for the protection of workers exposed to over 400 chemicals. This, however, has been overruled by the courts on procedural grounds.

The *Hazard Communication Standard*, also known as the "workers' right-to-know" rule, became effective in November, 1985. The rule requires manufacturers, chemical importers and all employers in the manufacturing sector (Standard Industrial Classification or SIC codes 20 through 39) to assess the hazards of chemical in their workplaces and to provide information to employees concerning their exposure to hazardous substances. This means of hazard communication includes labels, placards, *material safety data sheets* (MSDSs), training, and access to written medical and other records. In addition, distributors of hazardous chemicals are required to ensure that containers they distribute are properly labeled and that an MSDS is provided to the customer. The customers, as employers in the manufacturing division SIC codes, must in turn establish programs to educate their employees about these hazardous substances.

19.2.4 Consumer Product Safety Commission

Signed into law in 1972, the Consumer Product Safety Act provides for the creation of a five-member Commission (the CPSC), appointed by the President and confirmed by the Senate. The Commission must be bipartisan, containing no more than three members from the same political party, and it operates independently of any executive department. Products subject to regulation under the aegis of the Commission include those offered for sale for the personal use and enjoyment of residential, recreational, or institutional consumers. The Act does not cover products regulated by other Federal agencies, such as motor vehicles, tobacco, pesticides, aircraft, boats, food, drugs, and cosmetics. Children's toys and sleepwear are of interest to plastics compounders, and these are regulated by the Commission. The Poison-Prevention Packaging Act, administered by the CPSC, has proved a boon to plastics fabricators, since it provides that many of the safety closures on numerous potentially toxic household products be fabricated only with plastics materials.

CPSC was the first government body to strive for the banning of vinyl products that contain phthalate plasticizers because of suspected human carcinogenicity. Their Chronic Hazard Assessment Panel (CHAP) met on several occasions to consider action against di(2-ethylhexyl) phthalate, the net effect of which was an industry-wide voluntary incentive to remove DOP from all children's toys (or to limit it to no more than 3 percent of the product).

CPSC has banned all consumer products containing asbestos. Asbestos had long been used as a mineral filler for plastics, and at one time vinyl–asbestos tiles were the leading flooring material. Although the flooring industry has moved away completely from this product, there is still an appreciable amount of vinyl–asbestos flooring in residual use today. French researchers have claimed that during ordinary wear these tiles can emit airborne asbestos in important, health-threatening concentrations.

Flammability standards and smoke toxicity are high priorities with the Commission, which has issued a standard for the flammability of vinyl plastic film among others. Finally, the export of all consumer products banned in the United States is prohibited.

19.2.5 Non-Governmental Regulatory Bodies

In addition to the government agencies that have so much to do with the way our businesses are run, product standards are drafted as well by widely recognized non-governmental voluntary consensus organizations such as ASTM, ASME, and ANSI. Most specifications and testing methods for plastics products, including vinyl, are formulated by Committee D-20 of ASTM and are found in Volumes 08.01 through 08.04 of that organization.

The National Sanitation Foundation (NSF) is the major underwriting body for plastic articles going into food handling and potable liquid use. Although all municipal building codes do not adhere to NSF recommendations, most do, and the NSF label on one's plastic potable water pipe is a must. Their 1988 Standard 61, which includes health effects testing requirements, calls for leaching tests and determines whether the level and toxicity of migrants are acceptable from a public health point of view. The Standard is gaining rapid acceptance and puts plastics on a level playing field with other materials. For rigid PVC water pipe and other plastic pipe and tubing, NSF also requires hydrodynamic stress design testing before issuing their label.

19.3 CURRENT CONCERNS

19.3.1 Phthalate Plasticizers

Plasticizers for flexible vinyl, particularly the phthalates, became a *cause célèbre* in the early 1980s. Studies performed at the National Cancer Institute showed that di(2-ethylhexyl) phthalate (DOP) caused hepatocellular carcinomas and adenomas in both rats and mice at high feeding levels. Similar studies with di(2-ethylhexyl) adipate (DOA) disclosed that it, too, was carcinogenic for female mice (and probably for male mice as well), but not for rats of either gender. Although a bioassay of butyl benzyl phthalate indicated some evidence of carcinogenicity for female rats, other results were equivocal because of the toxicity of this plasticizer to the test animals.

The plasticizer toxicity issue is still with us, and although few restrictions in use have yet been proposed, all phthalates are under review by the EPA, with test data submitted regularly by industry groups under the Negotiated Test Rule provisions of the Toxic Substances Control Act. Nevertheless, DOP must still be labeled as a "potential" human carcinogen" according to the EPA, and that has eroded the market share of this plasticizer, particularly for vinyl floor coverings. The FDA is also considering regulations on the use of phthalate plasticizers in food-contact applications. However, low levels of human exposure due to migration into foodstuffs and the relatively inert character of these materials has kept the issue dormant in recent years. More recently, phthalate plasticizers have come under suspicion as estrogen mimics or endocrine disrupters (*loc. cit.*), even at extremely low levels of exposure.

19.3.2 Heavy Metals

Concerns about the effects of cadmium and lead heat stabilizers on human health and the environment, and the probabilities of replacement, date back at least three decades. Pressures to eliminate the environmental hazards ostensibly caused by lead exposure have led to the introduction of a Senate bill calling for reductions in commercial and personal consumption of lead and its compounds. The measures would ban lead in food processing and cans, phase-out lead in cosmetics and product packaging, and require 100 percent recycling of lead–acid storage batteries.

According to the Centers for Disease Control, even low levels of lead in young children result in decreased intelligence, as well as developmental and behavioral disturbances. The Lead Industries Association (New York, NY) warns that the proposed legislation could eventually lead to the banning of lead in other essential applications, such as PVC wire and cable. Color concentrate manufacturers are now warning their customers of the inevitable phase-out of not only lead pigments but also those containing cadmium and chromium. Many companies have stopped selling color pigments containing lead, cadmium, and chromium for plastics compounding.

Pending legislation may actually prohibit the use of these heavy metals in packaging, as exemplified by the recent announcements of the *Conference of North Eastern Governors* (CONEG). A special government–industry task force created in September 1989 by CONEG recommended specific legislation to CONEG's member States, which include Connecticut, Maine, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, and Vermont. Several states have already acted. Companies will be required to analyze their inks, dyes, and other packaging materials, and then remove toxic elements such as lead, chromium, cadmium, and mercury. There is growing environmental concern over heavy metal infiltration into landfill leachate and, to a much greater extent, its presence in incinerator ash. New York State has signed laws that restrict use and sale of chlorofluorocarbons and halons, but also ban heavy metals, particularly metal-based pigments, in packaging. The growing municipal solid waste problem has attracted the attention of Congress, where two bills were introduced into the Senate in 1989. These are the Solid Waste Disposal Act Amendments (*S. 1112*) and the Waste Minimization & Control Act of 1989 (*S. 1113*). Both bills emphasize source reduction and recycling as preferred methods for managing wastes, and provide some frameworks for achieving stated goals. But, among specific features of both bills are the banning of cadmium-based pigments (e.g., in plastics) and prohibition of landfill disposal of batteries.

Worker exposure to cadmium is another concern that increasingly absorbs the attention OSHA. OSHA had proposed a sharp reduction of the permissible exposure level (PEL) of cadmium in the workplace, which would lower cadmium levels by either 95 or 99 percent of the current $200\,\mu g/m^3$ of air PEL, to an average of 1 or $5\,\mu g/m^3$ of air per 8-hour TWA (time-weighted average). Excursion limits equaling five times these levels would be permitted for a 15-minute period. Action levels would be set at one-half the TWA PELs. The rule would cover 512,000 workers in a broad range of occupations and industries. OSHA estimated that the reduced PELs would prevent 4–14 cancer deaths and up to 189 cases of kidney dysfunction diseases per year, depending on the level set. Annual industry costs were put at $57 million to $160 million. But at OSHA hearings in mid-1990, officials said they may consider developing a separate higher worker exposure standard for cadmium compounds used in making pigments and stabilizers for plastics.

Finally, an EPA monograph on municipal solid waste in the United States is available, characterizing cadmium and lead products from 1970 to the year 2005.[23] Lead contributes 100 times more to MSW ash than does cadmium, and the primary source of each is battery disposal (cadmium from consumer Ni/Cd batteries). However, cadmium from PVC stabilizers and pigments used in plastics as a source is second only to that from batteries, according to the agency. There is considerable pressure on the vinyl industry to reformulate away from toxic heavy metals.

At present, there are no good substitutes for lead stabilizers in PVC electrical applications, although the search goes on (see, however, Chapter 4). Cadmium stabilizers, widely used for flexible and semirigid vinyl applications, appear to be phasing out in favor of barium/zinc, calcium/zinc, and zinc/polyphosphite systems. Performance capabilities of many of these packages leave something to be desired.

19.3.3 Estrogen Mimics

On August 3, 1996, the President signed into law the *Food Quality Protection Act.* Among other things, the measure repeals the infamous Delaney Clause, the four-decade-old amendment to the Food, Drug, and Cosmetics Act that banned carcinogens in food packaging, regardless of concentration or cancer risk. This signaled a shift away from the "cancer paradigm" of the past 40 years and a refocusing of health, safety, and environmental concerns on the effects of manufactured chemicals on endocrine systems. Although recognition of the role that chemicals play on reproductive responses is not new, the public is becoming increasingly aware and will undoubtedly demand more legislation and regulatory control of manufactured chemicals and the industries that generate them. We can anticipate that plastics additives, both as indirect food additives in food-contact polymers (regulated by the FDA) and as nonfood adjuvants that may migrate into the environment (regulated by the EPA), will be profoundly affected by new regulations targeting endocrine disruption effects.

The Safe Drinking Water Act Amendments of 1996 and the Food Quality Protection Act decree that pesticide manufacturers and some producers of other chemicals will have to test their product's ability to cause endocrine disruption. The water law requires the EPA to implement an endocrine disruption screening and testing program for chemicals found in drinking water, to which a substantial population is exposed, while the food law directs the same for all pesticides, both new and old. At this point, no-one really knows for certain how many chemicals or chemical manufacturers will be affected by the endocrine disruptor screening program.

Displacing our previous preoccupation with chemical carcinogenesis, estrogen mimics/endocrine disruptors will be the focus of intense environmental concern for the next decade. These ubiquitous and mostly synthetic chemicals masquerade as sex hormones, and extensive epidemiological evidence points to human fertility problems. They produce their adverse effects at very low concentrations. The young are especially at risk. Suspected estrogen mimics include the common phthalate plasticizers, alkylphenol-based surfactants, bisphenol A-based resin systems and certain persistent organochlorine compounds.[24]

Near-birth exposure of laboratory rats to small amounts of two endocrine-disrupting chemicals caused a 5–21 percent reduction in testicle size and daily sperm production on maturity, according to one study performed by the reproductive biology unit of the U.K. Medical Research Council (MRC). Rats were exposed to one of the compounds, the plasticizer butyl benzyl phthalate, at a level 300 times below that previously thought necessary for testicular toxicity, and yet the abnormal response was invoked. The other chemical was *p*-octylphenol.[25] Toxicologists have only recently discovered the possible estrogenicity of other widely used chemicals, such as bisphenol A, other phthalate esters, and additional alkylphenolic compounds.[26]

French scientists have reported a decline in the sperm count of Parisian men between 1977 and 1992,[27] although a control group in Toulouse showed no such regression. They attribute this to the supposition that industrial pollution is greater in the urban environment. Although not conclusive, evidence is strong that the estrogenic properties of phthalates, alkylphenols, and bisphenol A (from polycarbonate plastics and food can linings) may be responsible. Chemical firms are now developing reliable and repeatable assays for environmental estrogens and endocrine disruptors.[28] The EPA held a workshop on endocrine disruptors in Raleigh, NC, in 1995. As well as establishing a forum for discussion, the agency hoped to develop a national strategy for addressing these newly publicized and strange phenomena, ostensibly caused by simple chemicals (including dioxins).[29]

Bisphenol A (BPA), a constituent of polycarbonate resins, has been linked to human reproductive disorders as an “environmental estrogen.” The FDA and a plastics industry consortium have conducted a study to determine if possible migration from polycarbonate food packaging poses any risk under extreme conditions. Under severe stress, 30 minutes of boiling a mixture of 10 percent alcohol and grape juice, only about 5 parts per billion migrated from the packaging to the liquid contained, while under a less stringent environment no extraction was noted.[30] BPA has been linked to enlarged prostates in mouse studies. Very low levels, which can leach from polycarbonate food and beverage containers, show estrogen activity in the rodents, according to scientists at the University of Missouri.[31] BPA was administered at 2 and 20 μg/kg of body weight during the 11th and 20th days of pregnancy, and male offspring had prostates 30–35 percent larger than controls. The Society for Plastics Industry (SPI) estimates that an individual in the United States potentially consumes 6.3 μg/day from the linings of cans.[32]

Butyl benzyl phthalate has also been identified as an estrogen mimic, as has di-n-butyl phthalate and the common food additive butylated hydroxyanisole (BHA) according to independent work performed by scientists in England, Spain, and Boston.[33]

Environmental activists are attacking the U.K. government for not calling for a phase-out of chemicals that mimic female hormones. A report by the MRC says that these estrogen masqueraders might be linked to testicular cancer and falling sperm counts. But the U.K. government wants more research before it acts. The MRC report found that deteriorating reproductive health in humans and wildlife might be connected with the many chemicals that either mimic estrogens or block the action of male hormone, but it stresses that a direct link has not been proven. Among suspected estrogen mimics are di(2-ethylhexyl) phthalate (DEHP) as well as alkylphenol polyethoxylate nonionic surfactants.[34]

Phthalate plasticizers have been under attack by environmentalist groups in the wake of a U.K. report by the Ministry of Agriculture, Fisheries and Food, which found traces of the material in baby formula milk, coupled with concerns about reproductive (estrogenic) effects. It was speculated that flexible PVC tubing plasticized with phthalates may have been responsible for the baby formula contamination, but the source remained obscure.[35]

The European Commission has placed chlorine in the category of "endocrine-disrupting chemicals" on their draft of a priority list of chemicals to be assessed under the European Union (EU) regulation of evaluating and control of existing substances. The draft was distributed to industry and EU governments. According to Greenpeace, the evidence is such that all major uses of chlorine should be phased out by 2005.[36]

As an interesting sidelight, estrogenic substances in domestic sewage come from human rather than manufacturing sources. According to the U.K. Environmental Agency's Chief Scientist, the water industry should invest in research to assess the sources, fate, and behavior of hormones in the sewage treatment process, although he stressed that treatment does not remove most of the total hormone burden from effluent. Hormones present, however, were in a biologically active form, and these were found to cause male rainbow trout to produce the egg yolk compound vitellogenin normally found only in female fish. A search for the pollutants responsible turned up only three hormones (found in women): estradiol, estrone, and ethynylestradiol.[37]

Scientists at the National Institute of Environmental Health Sciences report that a set of three existing tests, when used in combination, provides a rapid assessment of a chemical's potential to mimic the hormone estrogen. One test determines whether the chemical can bind to an estrogen receptor site; the second determines whether it activates estrogen-responsive genes in a cell line; and the third determines whether the chemical causes the proliferation of estrogen-responsive uterine tissue in female mice. Using these tests, results can be obtained in 3–5 weeks at a cost of about $15,000, versus $1–2 million for conventional cancer bioassays.[38]

The EPA has also announced the availability of the *Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis*, which cedes that no conclusive evidence has emerged that industrial chemicals disrupt hormonal systems in humans. The report provides an overview of the current state of the science of endocrine disruption. Its major components are an introduction to the endocrine and the endocrine disruption hypothesis; a review of potential human health and ecological risks; and an analysis section, including an overview of research needs. The agency has found, except for cases involving workplace exposure, that there has been no causal relationship shown between these chemicals and hormonal disruption leading to adverse health effects. Nevertheless, the EPA said such chemicals have been shown to disrupt hormonal activities in animals and pose a potential risk to humans, so research into so-called endocrine disrupters should be stepped up. The report represents a summary of a more extensive review issued by the National Academy of Sciences in 1997. An electronic version is accessible on the EPA's Office of Research and Development (ORD) home page at http://www.epa.gov/ORD/. It can also be obtained by contacting the ORD Publications Office, Technology Transfer Division, National Risk Management Research Laboratory, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268; telephone (513) 569-7562; facsimile (513) 569-7566.[39]

19.3.4 Polyvinyl Chloride

Environmental activist groups have maintained a steady campaign to eliminate the production and use of PVC-based polymers (see the Clean Water Act, *loc. cit.*). Echoing Greenpeace, the 30,000-member American Public Health Association (APHA) has called for industry to prove that the risk from chlorine-based organics is "insignificant or lower than alternatives." The group also urged "measurable and progressive reduction toward elimination" of chlorine-based bleaches in the pulp and paper industry. But industry is mobilizing a counteroffensive, and both the Canadian and U.S. governments have rejected the sweeping recommendations of the International Joint Commission. The Chlorine Chemistry Council says it does not oppose, but does not endorse, APHA's call. In their counteroffensives, the American Chemistry Council (ACC), the Chlorine Institute, and the Vinyl Institute hope to neutralize this extreme view, which appears to be fueled more by public relations than hard science. Norway has commissioned researchers at MIT to study the policy and the economic implications of a total chlorine ban.

Greenpeace and its activist allies remain determined to cripple the PVC industry, alleging that vinyl's production and disposal create toxic chlorodioxins. And while the general vinyl industry is marshalling its forces to respond to the dioxin issue, flexible PVC suppliers and processors could be dealing with even more questions. Environmental concerns have been raised about each of the four major chemical components of flexible PVC: PVC resins, phthalate ester plasticizers, heat stabilizers (which often contain "heavy" metals), and pigments that include lead chromates. Phthalate esters, the additives that make vinyl flexible, have been linked in some literature to endocrine disruption—a broad term that covers disorders in the reproductive process of humans and animals. Lead chromates are used in the vinyl industry as pigments, especially the red, yellow, and orange shades. Lead chromates are regulated along with pure lead, even though as solid insoluble compounds they do not present the same level of hazard, and regulations require workers to use special protective gear. Rigorous cleaning procedures must be followed in plants using the pigments in powdered form. The alternatives to lead chromate and other toxic pigments are discussed in Chapter 5. Heat stabilizers used to prevent the degradation of vinyl products during processing often include toxic heavy metals, all of which have come under some form of regulatory scrutiny. Elimination of toxic metals from heat stabilizers is discussed in Chapter 4.

The most probable reason behind Greenpeace's intense effort to curtail vinyl manufacture and usage is that PVC production consumes a major amount of all chlorine made. If PVC were eliminated, the market for chlorine would possibly evaporate, along with concurrent production of caustic soda. The effect on the entire chemical industry could be catastrophic, and its collapse could be envisioned.

19.3.5 High-Production-Volume Chemicals

Over the past decade, the modes of environmental risk assessment have undergone great changes in the United States and Europe. In the United States, chemical testing has evolved from a command-and-control regulatory policy to a more collaborative model, while just the opposite has happened in Europe. These transformations are associated with changes in the relationships between governments, the chemical industry, and environmental nongovernment organizations (NGOs).

The high-production-volume (HPV) chemical testing program had its genesis with a 1977 study by the Environmental Defense Fund (EDF), an NGO. EDF reported that little or no data was publicly available on the health or environmental impacts for 75 percent of over 3000 chemicals that were produced in quantities greater than one million pounds per year. Much of this information did exist in the files of chemical manufacturers, but this was not generally available to the general public. EDF's findings were confirmed by industry, which voluntarily began a series of meetings with the NGO to negotiate uniform standards of HPV testing and data publication.

In 1988, the EPA, industry, the Organization for Economic Cooperation and Development (OECD), and various NGOs agreed to publish a data for each chemical as well as an expert assessment of the hazards associated with each. Later that year, the ACC, EPA, and EDF had agreed to a cooperative testing program. Chemical manufacturers formed smaller partnerships to test the various classes of compounds. The new HPV testing program alarmed animal rights activists when it was disclosed that an average of about 500 animals would be killed per compound tested. Efforts followed to reduce the mortality of test animals, and eventually the HPV program was able to accommodate most of the changes demanded by these activists and yet retain its focus on producing more data about chemicals and making it publicly available.

Meanwhile, the EU has adopted a stiffer approach to testing and regulation. Under consideration is a policy that calls for extensive industry testing and submission of resultant data to government regulatory bodies, which would authorize marketing or reject manufacturing and import, all before the product hits the market. The most recent program proposal, Registration, Evaluation and Authorization of Chemicals (REACH), calls for safety assessment of all chemical substances and their products. Although REACH has not yet been approved and is currently under revision, the final program is most likely to retain a centralized regulatory focus with the explicit goal of forcing substitutions for toxic substances, in many cases regardless of cost.

19.4 REGULATORY REFORM

Most regulatory reform measures introduced in Congress have bogged down under recent administrations, which promise a Presidential veto. In an attempt to derail partisan legislative initiatives, administrative reforms have been proposed, aimed at easing regulatory burdens, especially for small businesses that unintentionally violate the rules. These reforms include general government-wide measures as well as specific ones targeting the EPA and FDA. Such measures do not require Congressional approval. This plan called for allowing regulators to waive a small-business fine for first-time violators as well as for those businesses that spend a comparable amount on correcting the violation. Business reaction to the White House initiative was mixed.

19.5 PRODUCT LIABILITY

The House of Representatives passed a measure aimed at limiting “frivolous” lawsuits by making the loser pay legal costs under certain conditions. The body voted 232 to 193 to approve the bill, the first in a package of three proposed changes in the nation’s civil litigation system. The *Attorney Accountability Act* would require parties in many Federal lawsuits to pay the other side’s legal fees if they refused a settlement offer and eventually received less through trial. The vote occurred against a backdrop of bitter acrimony and competitive lobbying campaigns by business, consumer and legal groups as well as a strong protest by the Administration.

The second House bill, the *Securities Litigation Reform Act*, designed to limit suits by shareholders alleging fraud against companies whose stock price had dropped and setting standards forbidding “reckless” statements to deceive investors, was approved shortly thereafter. This bill would have little effect on the plastics industry.

The third House bill on product liability reform, the Common Sense Legal Standards Reform Act, was approved by a vote of 265 to 191. It limits the liability of retailers who sell defective products to the portion of damages caused by their own actions; abolishes “joint and several liability” for “pain and suffering” and other non-economic damages; shields drugs and medical devices approved by the FDA from punitive damage awards; prohibits suits over injuries from a product manufactured and sold more than 15 years previously, unless the product was expressly warranteed for a longer period (or it involved a chronic illness that takes longer to become evident); and limits punitive damages in all state and Federal civil suits to $250,000 or three times the amount of economic loss, whichever is greater.

A more moderate bipartisan product liability bill was introduced in the Senate. This legislation does not require losing parties in a lawsuit to reimburse adversaries for legal expenses and does not include a cap on noneconomic “pain and suffering” damages. However, the House’s cap on punitive damages is retained, as well as new protection for retailers and wholesalers. This bill was more favorable to the Administration.

Congress also passed landmark “unfounded mandates” legislation to discourage the regulatory agencies from imposing new, costly requirements on state and local governments. The House had approved the bill by a vote of 394 to 28 and the Senate, 91 to 9. If the annual cost of a new mandate proves to exceed $50 million for states and localities, or $100 million for private interests, the accompanying regulation would be subject to a point of order in Congress, which could then waive it by a simple majority vote.

19.6 RESPONSIBLE CARE

The 15-year-old U.S. Responsible Care program established by the Chemical Manufactures Association, now called the American Chemistry Council (ACC), was established as a proactive response to government legislation and regulation of the chemical industry. It has more recently taken on security and verification issues as keys to enhancing its longevity and reputation in response to the terrorist attacks on the United States on September 11, 2001. Third-party verifiers will have to certify the environmental health and safety management of all 169 ACC member companies, and new verified security measures must soon be put into place to ensure the security of chemical plant sites. Much of ACC's activity around Responsible Care and its programs is to counter criticisms from environmental groups such as Greenpeace. Ever since the terrorist attacks and the new sense of vulnerability they brought to the country as a whole, ACC has been preoccupied with security. The entire issue of verification, both for security and for Responsible Care overall, is a thorny one. While ACC has committed its member companies to the program, it is still not really clear to some members how valuable such a verification program is. ACC tossed out an earlier voluntary management systems verification program; it seemed to have little respect. Members must now submit to mandatory third-party audits. Aside from the security inspections, which are still loosely defined, ACC now requires all members to undergo one of two types of third-party audits by the end of 2007. The first, Responsible Care 14001 certification, lays Responsible Care's health, safety, and product security requirements over ISO 14001 environmental management assessments. ACC collaborated with the U.S. Registrar Accreditation Board to create RC 14001. Firms may also choose to undergo a Responsible Care Management Systems (RCMS) audit with independent auditors sanctioned by ACC. The goal of Responsible Care is to "create a better, safer, and healthier world" with the new security code and verification systems contributing to that effort.

The Canadian Chemical Producers' Association (CCPA) has required mandatory verification of the Responsible Care ethic since 1993, and its experience has been very different. The International Organization for Standardization and its ISO management standards have no credibility with labor unions, environmental activist groups, or even with parliamentary leaders. Of the two public verifiers doing the inspection, one is from CCPA's national advisory panel and one is from the local community where a facility is being inspected. The other two verifiers are from industry: one may be a retired chemical industry executive and the other a retired Responsible Care coordinator. By contrast, ACC's new verification programs pointedly do not include industry representatives because they are meant to be true third-party inspections. Public representatives may observe the process and may be invited to comment but they are not essential players in the inspection.[40]

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CHAPTER 20

Formulating Flexible PVC for Molding and Coating

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20.1 POWDER COATING AND MOLDING

Useful articles made from PVC powder include fluidized bed coatings for dishwasher racks, jumper cable clamp handles, automotive coil springs, lobster traps, pharmaceutical bottles, poultry watering dishes, low-voltage bus bars, and tool handles. Larger items, such as appliance grills, are usually coated instead by electrostatic spray. Some products, such as coatings for wire for fencing, outdoor furniture, fence posts, and scuba diving gear, can employ either fluidized bed or electrostatic spray, depending largely on the preference of the manufacturer. In recent years,

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automotive instrument panels have been produced in which the underlying polyurethane foam is coated with PVC using powder compound.[1] Most of these processes compete with plastisol coating or slush molding. They are, in fact, referred to commonly as "drysol" or "powder slush" molding. In comparison with analogous plastisol applications, powder coating or molding often offers convenience and, in some cases, performance advantages. Volatility and odor of the final product are typically reduced because of lower plasticizer content. With increasing concern over emission of volatiles to the air, powder coatings are likely to gain market share.

20.2 DEVELOPMENT OF POWDER FABRICATION PROCESSES

Powder fluidization dates to the 1920s, mainly from the work of Fraser.[2] Its application to coating of substrates with polymers did not become more than a specialty technique prior to the invention of the fluidized bed by Erwin Gemmer in the 1950s. The original patent remains worth reading as a model of lucid writing.[3] Fluidized bed processing was made practical by the recent appearance of porous stainless steel sheet, fabricated by sintering in a reducing atmosphere. This provided an ideal container, permeable to gas or air but able to contain powder of all types. Sintered metal sheet was pioneered in the United States by the Pall Filter Co.

The technique was originally applied to polyolefins, where a number of grades of resin were available in fine powders. Patents on fluidized bed coating of PVC powder do not appear until 1970,[4] although it is generally thought that commercial use began a decade earlier. Electrostatic spray coating of polymers also became widespread in the 1970s, adapting paint spraying methods.[5] Use of PVC powder, in this case, emerged immediately.[6] These methods replaced less attractive procedures, such as dipping hot metal substrates into containers filled with nonfluidized powder (fixed-bed coating) or coating powder with a knife or bar across a heated substrate. As a result, the range of application was broadened. The advantages in comparison with plastisol, organosol, or solution coating of PVC are:

- Reduced emission of volatiles
- High output as a result of fast cycle time
- Rapid clean-up
- Generally better compound shelf life
- Often lower compound cost
- Wider formulating versatility
- Potential for improved properties through use of higher-molecular-weight resins

The powders used were originally produced by cryogenic grinding of melt-compounded PVC.[7] A product of the order of 50-mesh was typical. The advantage of cryogenic grinding is that a broad range of PVC formulations may be employed, as long as the final grind is, or can be partitioned into, a stable, more or less free-flowing powder. The disadvantage is that the addition of a grinding step is unattractive economically. It is used today in situations where the value added in the product justifies the added step, where a suitable dry-blend powder is difficult to make or store, or where the manufacturer has the grinding equipment and therefore persists.

20.3 PVC POWDER COMPOUNDS

A greater part of the PVC powder for coating is today produced by dry-blend compounding.[7] Whereas with melt compounding, PVC resins ranging from an inherent viscosity (IV) of 0.52 (*K*-value 51) to 0.95 (*K*-value 68) have been used, recommendations for dry-blend compounding are often limited to the 0.70–0.90 IV range.[8] In order to flow together in fusion without applied pressure or shear, the suspension PVC resins (which are mainly used in dry-blending) should mimic the properties of a bulk resin; that is, have relatively high porosity, rather than a tough exterior grain surface. Irreversible plasticizer take-up (IPTU) should be in the range of 0.28–0.40 for most applications.[9] Special techniques have been used to prepare such resins.[10]

Resin particle size and shape are also important. Compounds for electrostatic spray should be dry-blended from resins in the 30–90 μm range, having a relatively narrow size distribution and a roughly spherical shape (to maximize retention of the static charge). Those for fluidized bed coatings (usually heavier than spray coatings) are based on resins in the 75–150 μm range, again of relatively narrow size distribution, to avoid stratification based on particle size occurring in the bed. Almost all powder coating compounds also contain 2–5 parts per hundred of resin (phr) of a dispersion resin (IV 0.8–1.1, *K*-value 62–73). These fast-fusing, fine-particle resins, in addition to promoting rapid coalescence, act as partitioning agents for the compound, improving fluidization and flow.

Although occasional reports of powder coating of unplasticized PVC are found in the patent literature, commercial applications are limited to semirigid and plasticized compounds. Choice and level are dictated by the application, to be discussed in following sections. Similarly, such compounds may use organotin or liquid mixed metal stabilizers, depending on the application. Automotive instrument panel (drysol) molded coatings, on the other hand, typically use powdered mixed metal stabilizers because of severe fogging resistance requirements. With the exception of large-volume applications (e.g., fluidized bed coating of dishwasher racks), filler and pigment loadings are generally held to 10 phr or less in the interest of promoting rapid fusion.

20.4 DRY-BLEND PROCEDURES FOR POWDER COATING

A mixer or blender equipped with a heating jacket is preferred; a typical starting temperature is about 200 °F (93 °C). The charge includes the suspension resin, stabilizer, and all nonlubricating solids. Mixing should proceed until the batch reaches 120–130 °F (49–54 °C). If the blender does not have a heating jacket, the solids, of course, will be at ambient temperature, and the plasticizer must be preheated so that the batch temperature reaches 170–180 °F (77–82 °C) after liquid addition.

Power draw can be used to monitor the dry point (at which plasticizer uptake is complete) usually at 180–220 °F (82–104 °C) for monomeric and 210–240 °F (99–116 °C) for polymeric plasticizers. Additives contributing lubricity may be added at this point. The batch is then cooled, either by means of the jacket or by transfer to a second blender or mixer, to about 120 °F (49 °C). After cooling, the small fraction of dispersion resin is added and mixed for several minutes. With some compounds, it is preferable to use a cooled high-intensity mixer for this step, since uniform distribution of this ingredient is key to good appearance of the final product. A suitably equipped high-intensity mixer may be used for the entire procedure. Finally, the powder compound is screened through a 30- to 40-mesh screen to remove agglomerates or contaminants.

20.5 SUBSTRATE PREPARATION

Metals that are to be PVC powder-coated are expected to furnish parts having good appearance, flexibility, toughness, and durability. It is anticipated that the metal will then be highly corrosion-resistant. Although a number of metal preparation procedures have been used, the most common now in practice is the "seven-stage" system comprising alkali wash, water rinse, acid pickling bath, water rinse, zinc phosphate anticorrosion coating, water rinse, and dilute chromic acid rinse. In addition to dirt removal and addition of an anticorrosion layer, this process provides a receptive, slightly roughened surface.

If high adhesion to the metal substrate is needed (e.g., with dishwasher racks), the cleaned metal is also primed. At one time, primers were based on solution coatings of flexible polyacrylates mixed with epoxy resins. The primers used now are most often acrylics that have been copolymerized with epoxide monomers, such as glycidyl methacrylate. These are formulated into proprietary adhesives, both solvent- and water-based, incorporating delayed-action epoxy curatives.[11] There have been many efforts to avoid the use of primers, including special purpose PVC resin copolymerized with epoxide monomers,[12] incorporation of primer ingredients into the PVC compound,[13] and development of unusual stabilizers that are also coupling agents.[14] All of these may find some specialty uses; most applications requiring metal adhesion still use primer coatings.

The fixture that holds the part during electrostatic spraying must be conductive so that the part is grounded; this is not necessary with fluidized bed coating of discrete parts. In other respects, a great deal of ingenuity has gone into the design of jigs and fixtures to promote easy re-use.[15] At the present time, the most common practice is to use part-holding fixtures and jigs that provide the greatest line speed and output, and then pass these through cleaning solution baths for reclaiming. The use of masking, generally with heat-resistant tape, of areas where powder coating is not desired has similarly decreased, making use instead of design features where areas that need not be coated are used for part holding. Where need be, uncoated areas are touched up with hand-applied plastisol coatings.

In most fluidized bed production lines, fixtured parts move continuously through cleaning and priming stations to a preheating oven, most often a recirculating convection type, either electric or gas-fired. Infrared and induction heaters are also used. Ovens are typically set at 400–600 °F (204–316 °C), depending on the application and heat capacity of the part. With relatively thin coatings (low pickup in the fluidized bed), high substrate temperature can greatly reduce postheating requirements. Oven time and temperature must be adjusted to coordinate with the fluidized bed coating cycle. For example, a steel panel, heated such that it contacts the PVC powder compound at a surface temperature of 450 °F (232 °C), picks up, we shall assume, a coating 300 μm thick in 5 s. Increasing the heat input so that the metal surface is at 500 °F (260 °C) will result in a thicker coating after 5 s exposure, say 450 μm. Or the 450 μm coating might be achieved by an exposure of 20–25 s at the lower temperature (with poor thermal conductivity typical of the compounds, the increase in coating thickness tends to drop off exponentially with increased exposure time). Thus output favors increased heating of the substrate. This, of course, is limited by the heat history that can be applied to the compound and primer without onset of degradation. Primer coatings of low thickness (2–5 μm) have been found to have greater resistance to degradation during preheat than thicker coatings (10–20 μm).[16]

20.6 FLUIDIZED BED OPERATIONS

The fluidized bed described by Gemmer is still standard. For PVC powders, dry air is satisfactory (the moisture content of the compound should be held below 0.5 percent). The plenum chamber into which compressed air enters is designed for streamline flow. The porous plate through which it passes to fluidize the bed may be of sintered stainless steel or ceramic composition, with controlled pore size typically one-tenth that of the powder compound. In some cases, the fluidized bed is equipped with a mechanical vibrator to assist in fluidization. In many operations, provision is also made for the part to move up and down or from side to side in the bed. This is often important in obtaining a uniform coating at intersections, edges and corners.

In practice, both circular and straight line process lines are used. Dipping in the fluidized bed is almost always followed by air brush removal of excess powder, then by a postbake to complete fusion. A postheat cycle is commonly 1–3 minutes at 400–600 °F (204–316 °C). If multiple passes are used, for example for heavy coatings (500–1500 μm), a postheat cycle follows each dip. In many cases, final postheating is followed by an accelerated air or water cooling step to speed unloading of parts.

In the continuous powder coating of wire—most often for fencing, but occasionally for insulated cable components[17]—it is advantageous to use electrostatic fluidized bed devices. In these, electrodes are embedded in the fluidized compound and a ground plate is mounted above the bed. This produces a cloud of charged compound particles above the actual bed, permitting the wire (also grounded) to be run continuously above, rather than through the bed using seals. This process is practical only for continuously running articles (in practice, it is limited to pipe and wire). In applications where it is important that the coating be continuous but the thickness of the coating can vary to some extent without ill effect, powder coating of wire becomes competitive with extrusion. This results from the lower cost of the wire handling equipment needed to produce a functional product. It is most often the case with steel wire for fencing, where the heavy gauge of the "conductor" would require a large investment for conventional extrusion. In electrostatic fluidized bed coating, substantial chatter and vibration and of the wire during coating does not cause any great difficulty. With traditional extrusion, this must be eliminated to prevent development of bare spots (and excessive equipment wear).

Fluidized bed operations using PVC are relatively clean. The compounds are typically difficult to ignite. Nevertheless, precautions must be taken to avoid inhalation of dust or its emission. In particular, powder lost from the bed, or excess removed by an air brush, must be captured and preferably reclaimed. Both preheating and postheating ovens must be equipped with approved exhaust systems. The most potentially dangerous part of the operation is, however, not PVC coating, but metal preparation. Manufacturers are strongly advised to install widely available complete systems that build in appropriate worker safety and emission control features, rather than to rely on homemade devices.

20.7 ELECTROSTATIC SPRAY COATING

In this method, a fast-moving stream of compressed dry air sucks PVC powder compound into a spray nozzle, where a high-voltage electrode (typically 70–90 kV) imparts a negative charge to the particles. Grounding the suspended part draws most of the charged particles to its surface, at least with the spray gun in the hands of a trained operator. In comparison with fluidized bed coating:

- Metal preparation is the same.
- Primers must similarly be used for metal adhesion.
- Usually, the part is not preheated (but see below).
- Typically, the coating is lighter than with a fluidized bed. A heavier coat can be obtained by preheating the part.
- At equal coating weights, lack of preheating leads to longer postheating cycles. In practice, lighter coating weights remove this disadvantage.

Fluidized bed coating is generally faster, easier to automate, less dependent on worker skill, and more likely to provide better consistency than electrostatic spray coating. It is, however, more demanding in terms of capital investment. Electrostatic spray predominates where parts are large and unwieldy, and where manufacturers do others types of spray coating. These considerations combine in the production of PVC-coated appliance grills and racks.

20.8 CONTINUOUS SPRAY COATING

Metal conduit and pipe, the latter for fence posts and outdoor furniture, and also for gas transmission, are PVC powder-coated both by fluidized bed and by electrostatic spray techniques. With fluidized bed coating, the most common procedure is to use an electrostatic bed, as with wire, so as to pass the substrate over, rather than through, the bed. The latter is also in practice, using seals. The entrance seal, contacting the primed metal, must resist heat and abrasion. In addition, the coating must fuse in the bed to a sufficient extent that it is not wiped off by the exit seal. The latter, of necessity, is not a tight seal, leading to powder loss and increased reclaim cost. Thus conversion to electrostatic fluidized bed coating is usually a good investment.

The automation of electrostatic spray coating of continuous substrates followed the development of analogous paint lines. In a typical installation, pipe is continuously coated by eight spray heads disposed equally around the perimeter, but staggered longitudinally. Each of the spray heads is adjusted so that very little overspray occurs, the multiple sprays then, in total, providing uniform coverage. Thus, exhaust requirements may be surprisingly low (based on experience with hand spraying) at this stage. Exhaust requirements for the surface preparation, primer coating and drying, and postheating stations are similar to those for continuous fluidized bed coating.

A single power system may draw the pipe through surface preparation, priming, drying, coating, fusion postheating, and cooling stations. Unlike hand spraying, continuous electrostatic spray coating is competitive in terms of output (and capital investment) with fluidized bed coating.

20.9 TYPICAL POWDER COATED PRODUCTS

Fluidized Bed-Coated Dishwasher Racks As these compounds may contain up to 25 phr of filler and pigment, and 50–60 phr of phthalate plasticizer (chosen for low odor and extractability), a resin of 0.85–0.95 IV is desirable. Nontoxic calcium/zinc stabilizers are used, with 4–5 phr of epoxidized soybean oil (ESO) and 2–4 phr of a dispersion resin.

Pipe, Conduit, and Fence Post Coatings These compounds typically use 5–10 phr of total filler and pigment and 20–35 phr plasticizer. This suggests the use of resins of 0.60–0.75 IV. Both electrostatic spray and electrostatic fluidized bed coatings should be free of antistats (e.g., glyceryl monostearate). Barium/cadmium liquid stabilizers have been used routinely, with ESO at 4–5 phr. In most cases, barium/zinc liquids could be substituted. From 2–3 phr dispersion resin is used.

General Purpose Fluidized Bed Coatings Tool handles, lobster traps, cable clamps, and so on, generally use low filler loadings to maximize output, plus usually 40–50 phr phthalate plasticizer and 5–10 phr ESO. Resins of 0.75–0.85 IV are typical. From 3 to 5 phr dispersion resin are used in these applications.

Barium/cadmium liquid stabilizers have been standard, but are being replaced with barium/zinc and calcium/zinc liquids. Similar clear coatings have, however, generally used organotin mercaptide stabilizers (except where odor is a consideration).

Appliance Grills (and Similar Products) via Electrostatic Spray These are similar to the above general purpose compounds, except that plasticizer content is at the lower end and dispersion resin content at the higher.

Electrical Coatings (Bus Bars and Cable Trays) These tend to be similar to the wire insulation coatings associated with them; that is, they use higher phthalate and trimellitate plasticizers, and lead stabilizers. In fact, the addition of 2–3 phr dispersion resin to the standard PVC insulation compound used with the coated article will usually generate the powder coating formulation.

20.10 POWDER SLUSH MOLDING

The development of increasing interest in, and intolerance of, odor and glass fogging in automotive interiors has led to a partial replacement of plastisol-coated polyurethane foam components, such as instrument panels, with powder-coated compositions. Although closer in detail to rotational molding of plastisols than to simple slush molding, the process is often referred to as powder slush molding or drysol molding. In the Japanese literature, however, the reference is usually to powder slush or rotational molding.[18]

In a typical operation, PVC powder compound is metered into a form that has been machined to a high finish to represent the desired part surface, then heated to a temperature at which the compound will sinter and partly fuse, while sufficient rotation is applied to obtain a uniform coating of the inside of the form. The latter may be, in fact, the same form previously used to rotomold PVC plastisol.[19] The polyurethane (PUR) component may be foamed within the form or, more often, prepared previously, placed in the form, and fusion of the PVC, with resultant high PUR adhesion, then completed.[20]

The compounds used are semirigid and, in some cases, ABS blends. In the case of a straight PVC compound, 30–40 phr of a low-volatility phthalate or trimellitate plasticizer is used. From 15 to 20 phr calcium carbonate is supplemented with 1 phr titanium dioxide, 1–2 phr antimony trioxide for improved flame resistance, 2–3 phr ESO, colorants as required, and about 0.1 phr (or less) stearic acid. The stabilizers used are barium/zinc or calcium/zinc powders supplemented with mineral acid absorbers and also a source of perchlorate anion. The latter is active in scavenging amine catalysts migrating from the PUR layer, which rapidly discolor PVC.[21] If need be, minor amounts of dispersion resin or of acrylic processing aid can be added to compounds such as the above to improve flowability. Although principally used in the United States for instrument panels, European and Japanese usage in arm and head rests has also been reported.

20.11 DIP COATING AND MOLDING OF PLASTISOLS

Dip coating and molding both refer to dipping a substrate into vinyl plastisol. If the substrate is a mandrel and is removed after the coating is fused, that is, if the plastisol itself becomes the article of commerce (e.g., a surgical glove), the process is plastisol molding. If the substrate (e.g., a polyacrylate windshield ice scraper, to be furnished with a soft hand grip) is retained, the process is plastisol coating. One should, however, be prepared for a certain amount of semantic overlap in practice.

These methods can be used to deposit tough, resistant coatings or moldings ranging from as low as 1 mil (0.025 mm) to over 125 mil (3.2 mm). In some situations, cold dipping of the substrate is possible. In this process, coating weight depends upon plastisol viscosity and rate of part removal. Cold dipping is used chiefly where the plastisol is of high viscosity (unless a low coating is desired) and—often the deciding factor—has low heat stability. For example, a heat-sensitive pastel colorant is used and high product consistency is needed. (This may arise when subsequently produced parts must exactly match others run weeks or months before.) In other cases, the substrate may be itself a thermoplastic with poor heat conductivity.

More often, however, the substrate is preheated. If the plastisol layer is to form a permanent coat and develop good adhesion to the substrate, the latter, if metal, must be primed (as described for powder coatings). Priming systems and application are entirely analogous. If, on the other hand, the fused plastisol must be demolded from the substrate, the adhesive primer is often replaced with an external release agent coating. Some applications are able to avoid this by use of a very fine surface mandrel as the substrate, by addition of internal release agents to the plastisol compound, or both. High-speed, automated lines, where rapid removal of a complex product is essential, such as with surgical gloves, often make use of all three means.

The preheated substrate, primed, release-coated, or neither, is dipped into the plastisol for periods of time generally ranging from 5 to 25 s, and withdrawn smoothly and slowly to control flow-off from the part. Substrate surface temperatures of 100–260 °C are common, running towards the low end if light coating weights of gelled but largely unfused plastisol are desired, and towards the high end to maximize pickup. Multiple passes are often used with hot dipping where high coating weights are needed. The general purpose plastisol compounds used in these applications tend to have gel points in the range of 65–80 °C.

Hot dipping will provide high output in an automated line, but introduces the problem of plastisol stability. Low-speed agitators and cooling coils should be used to limit heat transfer to the plastisol. Temperatue must be controlled for consistent results, as viscosity changes from temperature variation can affect appearance as well as coating weight. The compounds used should have the best possible viscosity stability. For hot dipping, compounds will typically use a blend of general purpose dispersion resin (IV of 0.9–1.15 and vinyl dispersion gauge of 30–40 μm) with 10–35 percent of a suspension blending resin (IV of 0.8–0.9 and vinyl dispersion gauge of 80–95 μm). Detailed recommendations are available from suppliers.[22]

Both cold- and hot-dipped parts are fused as with powder coatings. There is much variation in industrial practice regarding plastisol fusion cycles. Glass bottles coated with vinyl to prevent shattering on breakage are commonly oven-fused for 5–10 minutes at about 200 °C. Liquid mixed metal stabilizers containing organophosphites are used for heat stabilization. Less critical parts, such as low-end tool handles, may be fused in 30–40 s at 260–280 °C. Where fusion cycles are very short, zinc/phosphite liquid stabilizers may prove entirely adequate.

High-volume dipped parts such as tool handles and dish racks use automated lines as with powder coating. Plastisol dip coats are also used to decorate plastisol rotational moldings, notably in the production of multicolored traffic cones.

20.12 SLUSH MOLDING

Slush molding of plastisols is primarily used to produce rainboots and overshoes, and secondarily for toy and doll parts, and for automotive interior skin coats. The secondary uses are popular where circumstances such as short runs of many variations militate against rotational molding. The molds, typically low-cost aluminum, are preheated to a temperature at which the plastisol will gel rapidly, then filled with plastisol. After a brief gelation time, the molds are emptied of excess plastisol and placed in a fusion oven, then cooled to permit demolding.

In typical footwear operations, the process is automated. Excess plastisol is returned to the holding tank used for filling the molds. Low-speed agitation and temperature control are important to preserve plastisol shelf life. The latter are usually based on general purpose dispersion resins of IV 0.8–1.0. Initial viscosity, Brookfield 20 rpm, of 3000–5000 cP is preferred for rapid flow and good detail definition. Only a slight build in viscosity should be found on one day's standing. Despite the above cautions, considerable ingenuity has been exercized in diverting PVC regrind into such footwear.

A variation of slush molding in which the mold is filled with plastisol, but not then emptied of excess, rather the entire contents fused, is referred to as cavity molding. The major applications are for sink stoppers and fishing lures. Fusion is best carried out in long cycles, often 15–30 minutes at 175–190 °C, requiring considerable stabilizer demand. Stoppers and opaque lures usually use barium/zinc or calcium/zinc stabilizers. Clear solid molded products are typically organotin-stabilized. Both clear and pigmented compounds for lures often must have sufficient viscosity to suspend metal flake pigments.

A second variation of commercial importance is the in-place plastisol molding of automotive air filter components. Here, the paper air filter and supporting structures are placed in a ring mold (on one side of the assembly), and plastisol is added and fused. After demolding, the other side of the assembly is placed in the ring mold and similarly attached. With design ingenuity, the process runs semi-automatically.

In-place plastisol molding has been used for years to form gaskets for clay sewer pipe. A special assembly is placed over the end of the pipe, and plastisol is added and fused, using built-in heating elements. The PVC-gasketed pipe ends may then be joined readily with solvent cement.

20.13 ROTATIONAL MOLDING

Plastisol rotational molding is used to manufacture parts as diverse as doll parts, boat bumpers, mannequins, helmet liner and other sports protection components, sexual aids, traffic cones, and syringe bulbs. In this process, the exact part weight in plastisol is metered into a mold, usually automatically, and the mold is closed. During the gelling, fusing, and cooling stages, the mold is rotated by means of fixtures in two perpendicular directions, the path swept by the movement usually describing a sphere.[23] The molds used are most often cast aluminum; for best surface reproduction, powdered metal spraying can be used. Uniform mold wall thickness is desirable in aiding heat transfer; the molds are usually vented to improve strain relaxation, as well as to permit gas exhaust. The most common heat source is forced hot air, typically at 280–375 °C air temperature, for cycles of 5–10 minutes. Baffles and high-velocity air blowers are used to maintain uniform air temperature and avoid hot spots. In some cases, forced hot air is replaced with molten salt spray, usually at 200–300 °C. The improved heat transfer shortens fusion cycles notably, at the expense of investment in highly tight-fitting molds and the usual inconvenience of dealing with molten salts. This variation is typically used for molding heavy sections having a complex shape. Large single-mold apparatus for simple pieces (e.g., boat bumpers) can use direct flame impingement on the metal surface.

As with slush molding, plastisol viscosity should be low in order to achieve rapid part definition before gelling. In consequence, compounds typically use a mixture of general purpose dispersion resin and suspension or mass blending resin (the last, because of the absence of emulsifying agents, provides viscosity control without an associated increase in gelation time). Gelation time and viscosity stability also reflect the solvating power of the plasticizer used, with high stability but slow gelation reflecting low solvating power. The combination of choice of resin blend and of plasticizer can usually accomodate reasonable time–temperature fusion cycles.

Cooling during rotation can use forced cold air, water spray, or, in sophisticated systems, jacketed molds. Rotational molding builds in certain advantages over slush molding from the rotation itself; a very good surface appearance results from the constant strain relief during molding. Examination of molded parts shows that almost all defects are at the interior surfaces. Rotation must continue during cooling to preserve the best possible external surface.

Rotational plastisol and powder molding now compete in production of automotive interior surface layers for PUR foam structures (e.g., instrument panels, crash pads, and arm and head rests). Tooling and compound costs generally favor the use of plastisols, increased antifogging requirements the use of powders. Powder technology also opens this area to polymers other than PVC; future developments should be of interest.

In an interesting variation, plastisol can be injected into a closed mold with a positive displacement pump operating under low pressure. The mold(s) may then be placed in an oven, or may already be in a compression press equipped for heating and cooling. The major articles so manufactured are shoe soles, where the process competes with injection molding from pelletized compound.

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CHAPTER 21

Formulating Rigid PVC for Extrusion

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21.1 INTRODUCTION

Rigid PVC extrusion has emerged as the dominant process in the U.S. vinyl industry, currently accounting for over 70 percent of all PVC processed, not only for pipe but also for such building products as siding, window lineals, foamed pipe and profile, fencing, and sheet. Optimum extrusion of rigid PVC—both product quality and cost—is imperative to insure continued growth in existing markets and to permit development of new markets versus competitive materials. Understanding the proper selection—and use—of additives such as impact modifiers, process aids, fillers, lubricants, and stabilizers is a crucial part of developing an optimized extrusion process. Other factors that have significant effects upon the success of extrusion include compound blending procedures,

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proper matching of formulation to the extruder, and understanding the behavior of the extruder itself with its proper temperature and speed settings. The discussion will center on how these factors contribute to increased output rates while maintaining product quality.

21.2 PVC RESIN

Before considering the additives used in rigid PVC extrusion, the processor's primary material concern will be the vinyl resin itself—the major component of the formulation. For pipe extrusion, siding, and some profile extrusion, PVC homopolymer of medium or high molecular weight (K-value 65–70) is preferred. Good-quality resins are available via both the suspension and bulk polymerization processes. Other rigid extrusion processes such as foamed profile or sheet typically utilize lower-molecular-weight PVC homopolymer (K-value 58–62) or copolymers of vinyl chloride with vinyl acetate, ethylene, or propylene. These resins possess lower strength properties, but better melt flow and postforming properties. Whether resin choice is influenced by end-product requirements or processing needs, the importance of resin uniformity cannot be overemphasized.

Since most rigid PVC extrusion is from powder blends, and the extrusion process—especially twin-screw—is sensitive to powder blend properties of flow, compact density, and bulk density, the need to be aware of bulk density variations is most important. This awareness is especially necessary with the supplier's requirement to reduce the residual VCM content of PVC resin, which in turn can mean more severe drying cycles after a steam-stripping operation in the process. Consequently, the bulk density of PVC resin, and its particle size distribution, may be somewhat different now than previously—and the resin particle surface may be a little harder, or less absorptive to liquid additives. Many resins are much drier than before. In short, the dry-blend, powder flow, and bulk density differences of current PVC resins may require subtle changes in mixing procedures and extrusion conditions to maintain product quality (more on this later). Knowing this *before* the resin is blended and extruded can minimize a host of production problems.

Proper quality control of all incoming raw materials, especially PVC resin, is a must. Supplier Certificates of analyses on all shipments are necessary, and spot checks of moisture, bulk density, particle size distribution (percent fines), dry flow, heat stability, and fusion can be very helpful.

21.3 ADDITIVE SELECTION

Once the appropriate resin is selected, the compounder is faced with a staggering number of additive ingredients from which to choose. Pure PVC combines attractive cost with excellent physical and chemical properties. Any additive will change these properties and costs, since it is used for the specific purpose of enhancing either an end-use property or a processing characteristic of the PVC product. It is not only costly, but sometimes detrimental, to use more of an additive than is necessary to accomplish the intended effect. Therefore, the compounder must have a thorough understanding of the end-product requirements—physical, chemical, and visual—and must also be quite familiar with the particular extrusion equipment that will be used to produce the product: single- or twin-screw, die characteristics, and so on.

21.4 IMPACT MODIFIERS

Many rigid PVC extruded products—including some pipe, siding, window profiles, and sheet—require impact strengths beyond that attainable with PVC alone, which is a rather brittle polymer. The inclusion of a small amount of another polymer with a rubber "backbone" will, with proper dispersion into the vinyl melt, provide the shock-absorbing mechanism required to enhance impact strength of the PVC product by absorbing the energy of impact (measured as ft/lb in the crack propagating notched Izod test per ASTM D-256-72, or as a falling weight per ASTM D-2444).

Several types of specialty polymers will furnish the necessary marginal compatibility with PVC to function as impact modifiers. Chlorinated polyethylene (CPE), acrylonitrile–butadiene–styrene (ABS), methacrylate–butadiene–styrene (MBS), and certain acrylate polymers are the generic classes that are most commonly used. More recently, ethylene–vinyl acetate (EVA) has shown promise as an impact modifier. Each type offers its unique advantages—and disadvantages—which relate to weathering, clarity, effect on melt viscosity during processing, and heat stability. For example:

Weathering resistance	favors acrylates, CPE, EVA
Clarity and minimal stress whitening	favors acrylates, MBS, certain ABS types
Impact efficiency	favors MBS, ABS
Chemical resistance	favors CPE, EVA

Since impact modifiers are more costly than PVC, naturally no more should be used than necessary to provide required impact strength for the intended application. The relationship between use level and impact strength is not linear, but follows an S-curve as the effect diminishes past an optimum level.

Sufficient work input, or shear, must be achieved during extrusion to arrive at the optimum dispersion of modifier particles in order to obtain the maximum benefit from the quantity used. To achieve desired impact strengths for pipe, profile, and sheet applications, 2–5 parts per 100 of resin (phr), 7–10 phr, and 12–15 phr, respectively, are very typical use levels.

21.5 PROCESSING AIDS

Rigid PVC exhibits a very high melt viscosity and a tendency to stick to hot metal surfaces, resulting in uneven flow from a die opening, melt fracture, and frictional heat buildup to the point of degradation. Although proper lubrication is important, and will be discussed later, process aids can minimize these problems.

The concept of a "process aid" has contributed significantly to the development of all rigid PVC processes that depend upon shear: extrusion is no exception. The most widely used process aids are specialty acrylic polymers, which are used at 1.5–5.0 phr levels to:

1. Promote early, more complete fusion of the powder formulation
2. Contribute to uniform melt viscosity
3. Provide smooth flow from the die
4. Minimize die swell
5. Increase hot strength for string-up and draw-down to smaller sizes

Single-screw extrusion of rigid PVC definitely requires the use of a process aid to achieve optimum quality and production rates. Typically, 1.5–3.0 phr is sufficient. While not absolutely necessary in low-shear, twin-screw extrusion, the inclusion of at least 1.0–1.5 phr of a process aid definitely enhances product quality. Because of its effect on promoting powder fusion, a slightly lower barrel temperature profile may be used when running with a compound containing process aid on a twin-screw extruder.

21.6 FILLERS

Fillers are used in some rigid vinyl extrusion formulations as extenders for the prime purpose of reducing compound costs (cost per pound), but they also are used to achieve certain desirable end-use properties, such as an increased heat distortion temperature and stiffness. They are usually inert solids, taken from such classes of materials as alkaline earth metal carbonates and silicates, barytes, gypsum, alums, and even wood flour. The most commonly used chemical type is calcium carbonate, which comes in a variety of forms, including ground limestone of varying particle sizes, and specially purified precipitated grades—also of varying particle sizes. Some types are surface-treated with stearic acid or other additives to aid in processing, and these surface-coated "soft" fillers are widely used in rigid pipe extrusion, primarily because they are somewhat less abrasive than uncoated varieties. Abrasion in twin-screw extrusion is seen as screw and barrel wear.

In selecting the type and amount of filler for a rigid extrusion compound, several factors should be kept in mind: How much is necessary to achieve the desired improvement in tensile strength? Can I use less of filler A to obtain the same properties achieved with filler B? While lower cost per pound of PVC compound may be one reason to incorporate a filler, the cost of the filler—and finished compound cost—should be properly computed on a pound/volume basis, taking into account the differences in specific gravities of the various fillers—and their effect upon specific gravity of the finished PVC compound. The least expensive filler—or the higher use level of a filler—may not translate to lowest cost per foot of extruded product. Arriving at a choice of type and use level based on properties and cost, what effect will this filler have on the useful life of a set of barrels and screws, especially in twin-screw extrusion? Generally, filler levels below 5.0 phr (common for many pipe compounds) pose no real problem, but higher filler levels—telephone duct requiring high stiffness may contain up to 30 phr filler—will shorten significantly the life of barrels and screws. In fact, many extruder manufacturers will negate their warranty concerning screw and barrel wear at filler levels above 5.0 phr. Thus, if high filler levels are necessary, replacement costs for barrels and screws should be dialed into the overall economic analysis of highly filled rigid PVC compounds.

21.7 PIGMENTS

Pigments (and toners) are used primarily to achieve desired esthetic effects of the finished products. However, certain types (such as various grades of titanium dioxide) serve a very useful function as UV light reflectors to enhance the outdoor weathering life of the product. Being very inert and resistant to hydrolysis, oxidation, and extraction, titanium dioxide offers a very permanent approach to greater outdoor UV stability. Any rigid PVC extruded product intended for long-term outdoor exposure (siding, window profiles, etc.) normally should contain at least 8–12 phr of titanium dioxide. At these use levels, the effect on processing is much like a filler. Extruded pipe, most of which is intended for underground use, generally requires only 1–2 phr titanium dioxide. This amount is sufficient for the short-term light stability of pipe during outdoor storage prior to use—however, if longer-term storage or above-ground use is expected, the titanium dioxide content should be increased to at least 4–5 phr.

Other pigments—whether organic or inorganic—do not have any measurable effect upon the extrusion process, but there are "staining" types of chemical interactions that can occur between certain pigments and the atmosphere, or other additives. For example, many pigments are based on metals (cadmium, lead, iron, chromium, selenium, bismuth, cobalt, molybdenum, and manganese) that are capable of forming colored sulfides either upon exposure to sulfur-laden industrial atmospheres or by reaction with a tin mercaptide stabilizer. Pigments also possess varying degrees of UV stability during outdoor exposure—exhibiting bleaching, darkening, or color drift. Pigment selection should be made with at least an awareness of—and evaluation for—the above potential problems.

21.8 PLATEOUT

One perplexing problem that occasionally arises during long extrusion runs, especially with opaque, pigmented, or filled compounds, is plateout—a term used to describe the buildup or deposit of incompatible material on the screw, in the die, on roll take-up equipment, or on sizing sleeves. In time, this deposit affects the surface finish of the product, and also provides sites for sticking—leading to degradation. Production down-time for clean-up is then necessary. All the factors responsible for causing plateout are not fully understood. It is believed that minor incompatibilities of additives are partly responsible, but are not the whole cause. Changes in type and use levels of lubricants, fillers, pigments, and stabilizers, as well as changes in processing conditions (speed and temperature) can affect the severity of plateout—for better or worse. Even the weather (high humidity) has been known to aggravate plateout! Although plateout may occur in a clear formulation, most plateout incidents seem to happen with opaque, pigmented, or filled compounds. Invariably, a combination of two classes of metals are usually present in plateout-prone compounds: alkaline earths (calcium, magnesium from the filler, or barium from the stabilizer) and heavy metals (most commonly titanium from titanium dioxide pigment, also lead and cadmium from stabilizers or pigments).

Several empirical approaches to the control of plateout have evolved over the years, which have shown varying degrees of effectiveness. Stabilizers based on organotin derivatives have not been shown to contribute to plateout, mainly due to their very high compatibility or solubility in the PVC melt. On the other hand, salts of barium, cadmium, calcium, zinc, and lead are either insoluble or less compatible with the PVC melt, and can aggravate plateout if other conditions are right.

Compounds based on emulsion-polymerized PVC resins (E-PVC) normally cannot be induced to show plateout. In some cases, replacing a small amount (10–20 percent) of suspension (S-PVC) resin with E-PVC will reduce plateout. This may be due to the presence of trace amounts of emulsifier present on the resin, for the addition of either cationic or anionic surfactants in very small amounts (0.1 phr) has also been shown to reduce plateout.

A mechanical approach to plateout control that has worked successfully involves the use of a small amount (0.5 phr) of a silicate filler to contribute a mild abrasive or scrubbing action on metal surfaces.

A small container of mineral spirits mounted above the sizing sleeve of a vacuum cooling tank so as to permit a slow, dropwise addition of mineral spirits on the hot vinyl profile just before entering the vacuum sizer will often keep sizing sleeves clean.

21.9 LUBRICANTS

As mentioned earlier, molten rigid PVC has a tendency to stick to the hot metal surfaces of processing equipment, and also possesses a very high melt viscosity that can cause uneven flow from the die, melt fracture, stabilizer consumption from frictional heat buildup, high torque on the screws, and high back-pressures. If an optimum choice of all other formulation components is made without adequate consideration for proper lubricant balance, chances for successful extrusion are minimal. Unfortunately, our understanding of the science—or art—of lubrication does not measure up to its degree of importance. The critical need to unravel the nature of lubricity is especially important in rigid PVC extrusion, since it is difficult to completely separate lubricity and processing stability factors. Lubricants as additives can be separated into the following broad categories: fatty acids and alcohols; fatty acid amides and esters; metal stearates; hydrocarbon waxes; and low-molecular-weight polyethylenes. Silicones and other more exotic materials are occasionally considered for special applications.

Additive lubricants can be classified to some extent by relating their chemistry to behavior. The terms "internal" and "external" have been widely used (perhaps too much). A more accurate classification would view lubricant behavior within a broad, continuous spectrum—from the "internal" lubricity of polar molecules (stearic acid, metal stearates, and fatty acid esters) to the "external" lubricity of non-polar, long straight- and branched-chain hydrocarbon derivatives of paraffin oils and waxes and low-molecular-weight polyethylenes. Between these extremes can be found a number of lubricants possessing both polar groups and long hydrocarbon chains that—depending on the ratio of these groups—offer a variety of combined external–internal lubricant behavior to rigid PVC.

A lubricant's behavior is partly characterized by its effect on powder fusion and melt viscosity. Internal lubricants tend to promote fusion and contribute to a lower melt viscosity after fusion by reducing internal friction within the PVC melt (which is actually composed of discreet particles up to about 200 °C). External lubricants tend to delay powder fusion, and also migrate to the surface of the PVC melt due to their incompatibility, thereby reducing frictional drag between the PVC melt and hot metal surfaces of extruder screws, barrels, and dies. It is mainly this feature that helps to contribute a good surface finish to the extruded product.

Other additives—most notably stabilizers—can contribute to lubricity in rigid PVC extrusion compounds. A portion of most lead stabilizer systems consists of normal or dibasic lead stearate, while most barium/cadmium or calcium/zinc stabilizer systems are based on fatty acid soaps of these metals. These are all lubricating-type stabilizers; in contrast, organotin stabilizers are essentially nonlubricating—although some types can contribute slightly to overall lubricity. Most liquid organotin stabilizers can be considered as highly efficient plasticizers that promote fusion and reduce melt viscosity.

Rigid PVC extrusion compounds based on organotin stabilizers require about 1.5–2.5 phr of total additive lubricants, properly balanced for the type of extruder. Lubricant levels much beyond these extremes will result in either under- or over-lubricated conditions—seen as rough surface, sticking, melt fracture, and overheating in the former instance, or surging, lumpiness, and incomplete fusion in the latter. Much less lubricant is needed when lead, barium/cadmium or calcium/zinc stabilizers are used.

More recently, complete lubricant packages have been introduced that combine different types of external lubricant behavior with some internal characteristics. These systems are designed specifically for rigid PVC extrusion, and offer a balanced, single-component approach to lubrication that can result in greater economy and simplified compounding.

For most rigid extrusion applications, once the proper lubricant balance is established, selection is generally based on cost versus effectiveness. In clear PVC compounds, however, the lubricant's effect upon clarity must be considered. Metal soaps and most external wax-type lubricants are not entirely soluble or compatible in PVC, and one usually must rely on combinations of fatty acid amides and esters, which offer better clarity.

21.10 STABILIZERS

The total energy input that a vinyl compound experiences (especially rigid compounds) includes the shear and heat energy of mixing cycles, extrusion, fabricating (embossing, thermoforming, and laminating), scrap rework, and the heat and light energy of outdoor exposure. All contribute to PVC degradation, and the stabilizer system must furnish adequate protection at every stage during the production and service life of the vinyl product. Since appearance of color is indicative of degradation in PVC, the most reliable stability tests for extrusion involve assessing color development during dynamic processing—either on the extruder itself or in laboratory tests. Alternatively, PVC samples that have undergone dynamic processing of extrusion can be tested for residual stability or thermal abuse in a Metrastat-type continuous-exposure oven, and the visual color or UV-induced fluorescence that results can be measured on a scanning reflectometer.

21.10.1 Stabilizer Types

Basic Lead Salts Inorganic lead stabilizers were the earliest effective heat stabilizers for PVC. Litharge (lead oxide), the first lead compound to be used commercially, was soon complimented by a growing number of inorganic and organic lead compounds: basic lead carbonate, tribasic lead sulfate, lead silicates, dibasic lead phosphite, dibasic lead stearate, normal lead stearate, dibasic lead phthalate, and tribasic lead maleate. These compounds furnished inexpensive and effective stabilization to PVC. Leads are still used in PVC electrical wire and cable insulation due to their excellent electrical properties (low volume resistivity) and low water absorption. Pipe extrusion in many other areas outside the United States also provides a large market for lead stabilizers, and they find some use in opaque rigid vinyl extruded and injection-molded products. Sulfur staining, lack of clarity and the toxicity of lead stabilizers are drawbacks that limit their use. North American and European use is declining steadily as technology related to other types of stabilizers develops.

Mixed Metal Carboxylates Metal ratios can be varied to account for resin zinc sensitivity, filler content, early color or long-term stability requirements, clarity, and light stability needs. Barium/cadmium (zinc) soaps also offer some degree of lubrication at the expense of clarity in rigid vinyl extrusion or calendering. The barium component provides long-term heat stability, cadmium provides good early color and light stability, while zinc offers exceptional initial color (especially in highly filled systems) at the expense of long-term stability. Generally used in combination with phosphites and epoxy compounds, a well balanced barium/cadmium (zinc) stabilizer system can furnish good heat and light stability. Drawbacks of these stabilizers include the toxicity of cadmium, occasional plateout tendencies, and hydrolysis or leaching of soaps from PVC. Perhaps their biggest drawback in rigid PVC is the poor melt viscosity characteristics that they impart—a sort of melt stiffening. Stabilizers of this type in current use in flexible PVC in North America are now almost entirely barium/zinc or calcium/zinc. Technical advances have been such that cadmium usage is no longer necessary. There is almost no use of barium or cadmium in rigid vinyl in North America.

Calcium/Zinc These (often U.S. FDA-sanctioned) stabilizers, which are used in certain rigid PVC food-contact applications, are generally used with appropriate phosphite and epoxy secondary stabilizers to enhance their overall stability performance. Metal ratios can vary depending on product requirements, and other metals (magnesium, tin, aluminum, and sodium) can be added, but calcium/zinc stabilization is still difficult, providing minimal scrap rework capability. Film and sheet extrusion (flat die and blown film), and blow-molded bottles are some of the applications requiring FDA-sanctioned stabilizer systems. Hydrolysis of stabilizer components in contact with water- or alcohol-based products can cause hazing or "blushing" of clear PVC. This problem has limited the use of calcium/zinc in clear PVC applications. Research efforts in Europe and the United States currently center on development of calcium/zinc systems to replace leads in Europe and organotins in the U.S. rigid PVC markets.

Tin Carboxylates The earliest tin stabilizers, dibutyltin dilaurate and dibutyltin maleate, are typical of non-sulfur-containing stabilizers. These products, and subsequent developments in tin carboxylates, provided clarity to PVC and a much lower order of toxicity than lead- or cadmium-containing stabilizers. One stabilizer in this group, di-*n*-octyl tin maleate, is sanctioned by the FDA for rigid PVC food contact applications. Tin carboxylates are used in rigid PVC–acetate copolymer applications, but, in many high-output cases, do not offer the degree of stability required to process rigid PVC homopolymers. They do, however, exhibit excellent light stability properties, and are sometimes used in combination with the sulfur-containing organotins to enhance outdoor weathering capabilities of rigid PVC.

Tin Mercaptides The thio-organotins were introduced in the early 1950s and offered a considerable improvement in clarity and heat stability. Although they exhibited poor light stability and odor, tin mercaptides soon gained acceptance in the United States for the difficult stabilization of rigid PVC, and have been the most widely used stabilizers in rigid PVC pipe and profile extrusion, injection, and blow molding.

Tin mercaptides offer a unique set of properties for rigid PVC processing: classical vinyl stabilization and antioxidant functions combined with fusion promotion and melt viscosity reduction. Melt rheology studies have shown that, in addition to excellent color stability, organotin sulfur-bonded compounds furnish a lower melt viscosity in rigid PVC than structurally equivalent organotin oxygen-bonded compounds (tin carboxylates) of similar viscosity, molecular weight, and compatibility. They also impart lower melt viscosities than Group II A and B metal carboxylates (barium/cadmium and calcium/zinc stabilizers). Up to 1970, one particular organotin mercaptide, dibutyltin bis(isooctylthioglycolate), emerged as the dominant stabilizer in the rigid PVC industry. The quality of this stabilizer was refined over the years through improved color, purity and flash point, while later modifications of butyltin technology furnished still better color and processing stability to rigid PVC—the "high-efficiency" butyltin mercaptides.

During this period, di-n-octyltin bis(isooctylthioglycolate) was determined by the FDA to be safe for use in rigid PVC food-contact applications under conditions specified in 21 CFR 121.2602. Thus, for the first time, rigid PVC with glass-like clarity and sparkle could be considered for food and beverage packaging.

The tremendous growth of rigid PVC markets, especially of pipe and profiles, coupled with the increasing use of low-shear multiscrew extruders permitting lower stabilizer levels, prompted the development of lower-cost "mixed metal" barium/butyltin or calcium/butyltin stabilizer systems, which provided adequate processing stability for most low-cost, twin-screw extrusion formulations. Many of these, however, could not be run well on single-screw extruders, thus limiting their versatility.

Methyltin Mercaptides A significant improvement in rigid PVC stabilization technology was realized in 1970 with the introduction of methyltin mercaptides. The first methyltin stabilizer exhibited substantial cost–performance advantages over classical butyltin stabilizers in a variety of rigid PVC processes, and the most recent lower cost "reverse ester" methyltin stabilizer developments continue to show significant cost–performance advantages over both the high-efficiency and mixed metal butyltin mercaptides. These advantages include better initial color stability and color retention, higher output rates, and greater regrind latitude, obtained at lower cost. These new methyltin mercaptides are finding wide use in single- and twin-screw extrusion of pipe, profile, foamed profile and sheet, injection molding, and blow molding. Extremely safe to use, the new "third-generation" methyltin stabilizers possess surprisingly low acute toxicity levels—(LD_{50}: 4500–5500 mg/kg)—lower even than the earlier methyltin stabilizer that had obtained sanction for use in food-contact applications from many European authorities, including the BGA of Germany, as well as the FDA.

21.10.2 Stabilizer Selection

The basic type of stabilizer system selected is often dictated by end-use or regulatory constraints (NSF, PPI, FDA, and BGA). Subsequent choice of a specific stabilizer should be made with the major objective of achieving optimum cost–performance: How much processing stability is available per dollar of stabilizer cost? Or, conversely, what will be the lowest-cost choice to furnish the required processing stability for a particular process—including all safety factors such as regrind extrusion, power failures, and end-use stability needs? A level of stability much beyond the "necessary" level can translate to significant unnecessary costs. Laboratory tests (Brabender, mill stability, and Metrastat oven stability) can furnish an indication of comparative cost–performance, but the final decision really should be based on production extrusion runs and subsequent evaluation of either residual stability or regrind extrusion, which is also conveniently done on the Metrastat oven.

Within the organotin mercaptide group of stabilizers, the most recent “reverse ester” methyltin stabilizers have demonstrated a unique ability to impart extremely good initial color stability, and to hold that color during even 100 percent regrind extrusion to a much greater degree and at lower costs than were previously possible. In addition, as stabilizer level is reduced, the decrease in stability time (seen as color development) is much less with these new methyltin stabilizers than with butyltin or mixed metal tin stabilizers. This means that a given level of stability (necessary to run an extrusion plant including a regrind safety factor) can be achieved with less stabilizer in the compound. Typical use levels for twin-screw pipe extrusion are in the 0.3–0.4 phr range, and 0.7–1.2 phr for single-screw pipe extrusion.

21.11 MATCHING THE FORMULATION TO THE EXTRUDER

Single- versus Twin-Screw Extruder For any given rigid PVC extruded product, the choices of resin, impact modifier, pigment, filler, and type of stabilizer and lubricant system are dictated by the end-use or appearance properties required of the product, such as tensile strength, modulus, heat distortion temperature, impact strength, clarity, outdoor weatherability, and toxicity. Single- and twin-screw extrusion both achieve the same goal of producing a continuous shape out of a die, but the processing concepts involved are almost diametrically opposed. Therefore, important differences exist between single- and twin-screw formulations for the same product. These differences involve the amount of stabilizer, lubricant balance, and the amount of process aid. Here is a comparative view of process characteristics and formulation needs for the two types of extrusion:

PROCESS DIFFERENCES

Single-Screw	Twin-Screw
1. High rpm (25–80), high shear, higher melt temperature (200–225 °C)	1. Low rpm (10–40), low shear, lower melt temperature (185–200 °C), easier sizing from powder blend extrusion
2. Uneven melt temperature within a screw flight, nonuniform melt viscosity entering die, slight melt pulsation (surge) with each screw revolution	2. Uniform temperature within a screw flight, more even melt flow to die—primarily because of positive displacement “gear pump” action of counter-rotating, intermeshing screws
3. Lubricant balance—more internal to promote faster fusion, homogeneous melt, and lower melt viscosity; less external to minimize surging, slipping on the screws	3. Lubricant balance—less internal and more external, to delay fusion to metering zone in order to control amperage at maximum rpm. External lubricants, especially polyethylene, also prevent sticking and melt fracture in large-diameter pipe heads and dies

4. Process aid required to help develop uniform and lower melt viscosity	4. Process aid not essential—but low-level use will enhance product quality
5. Higher stabilizer level required, due to higher shear processing	5. Lower stabilizer levels possible, due to lower melt temperatures and lower shear processing

EXAMPLE OF FORMULATION DIFFERENCES

ASTM TYPE 1 PVC PRESSURE PIPE (CLASS 12454)—NSF

Single-Screw		Twin-Screw	
100	PVC (*K*-value 65–68)	100	
1.0	Titanium dioxide (rutile)	1.0	
1.0–3.0	Filler (stearate-coated calcium carbonate (0.7–2.0 μm)	1.0–3.0	
0.7–1.2	6–9% tin Methyltin stabilizer	0.3–0.4	
1.5–3.0	Acrylic process aid	0–1.5	
1.0–1.5	Calcium stearate	0.5–0.8	or lubricant blend 1.8–2.2
0.7–0.9	165 paraffin wax	1.0–1.2	
0.1	Polyethylene wax (oxidized)	0.2	

Keeping the lubricant balance the same, both of the above formulations can be changed to Type II pipe, conduit, or outdoor profile with the following adjustments:

Type II pipe	Add 4–6 phr impact modifier (ABS, MBS, or CPE)
Outdoor profile	Add 6–9 phr impact modifier (MBS, or CPE) Add at least 9.0 phr titanium dioxide Add 0.5 phr methyltin stabilizer Add 4–6 phr filler
Conduit	Add 2–3 phr impact modifier Use the higher level of process aid (for hot strength)

CHAPTER 22

Design of Experiments

R. J. DEL VECCHIO

22.1 BASIC QUESTIONS AND CONCEPTS

What is “Design of Experiments”? Doesn’t every scientist and technologist preparing to run an experiment have to organize or “design” that experiment before heading into the laboratory or factory? Didn’t Marie Curie and Thomas Edison and thousands of others make great discoveries without ever hearing of Design of Experiments?

There is no question that the Egyptians built pyramids, the Romans, aqueducts, the Chinese invented gunpowder, and the Wright brothers made the first successful plane, without Design of Experiments. So why is there need to study and understand this subject? What is it really about?

Simply put, Design of Experiments is a methodology for making experimentation maximally efficient. It is most useful when some phenomenon (chemical, physical, or a combination) to be explored is complex, in the sense of having several factors involved in the process. In a machining operation, these could be type of feed, process speed, alloy composition, use of cutting fluids, and so on. In plastics molding, the factors could be preheat temperature, injector barrel temperature, injection speed, and various aspects of mold design. In polymer product formulating, they might perhaps include polymer grade, use of polymer blends, level of plasticizer, use of antidegradants, processing aids, and so on.

Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman

If a process is simple enough, classic one-factor-at-a-time experiments make perfect sense. For instance, if one is baking bread and knows (has been told, has read in a book) that the oven should be set at 350 °F, but is not sure of the baking time, one can simply put in three loaves and take one out at 35 minutes, one at 40, and one at 45, and see which seems best. (This of course presumes knowledge that merely several minutes would be insufficient; that is, that the experimenter has a certain level of training and experience—always a good thing in vinyl formulating.)

On the other hand, if one is trying to optimize oven output, and would like to explore different baking temperatures, different baking pans, and different variations in flour to determine the shortest baking time leading to good bread, then that is a different matter. The baking process for one kind of flour might be a bit different than for another, so that the highest temperature and shortest time may not be the same. If the experimenter begins by merely looking for the highest temperature that will bake a single type of flour without singeing the loaf, and then uses that process time for all other types of flour and designs of baking pans, the answer resulting from the experiments is unlikely to be optimal.

The fact that one ingredient, flour, acts differently in regard to baking temperature than others is called an interaction, since two factors—flour and temperature—act in a coordinated way, instead of being completely independent in their effects on the baking process. Interactions are very common in chemical processes, which should be no surprise, since chemical reactions are forms of interaction in the first place. Detecting and quantifying interactions are a critical part of really understanding a process. Consider, for example, increasing filler level in a vinyl formulation. This will generally increase process viscosity. The result may be reduced output; in some cases, there may be no effect; in others, output may be improved. Now consider the effect of simultaneously increasing lubricant content. This again may or may not improve output. Suppose the lubricant (e.g., stearic acid) may or may not interact with a given filler. In this case, the magnitude of the interaction between ingredients is highly important to success in formulating.

Even when interactions are not significant in a given process, the one-factor-at-a-time approach still has many drawbacks. Among these is a lack of capacity for analysis of the extent to which process and measurement variability have affected the observed results. No process runs exactly the same every time, and no measurement technique is perfectly precise, so every result is associated with its own level of uncertainty. That means the result is only known to plus or minus some value, and—whether that variability is 1, 5, 10 percent, or more—cannot be determined or even approximated from single experiments. In many actual situations, it is very important to understand what the typical scatter is when interpreting experimental results. Designed experiments always provide information on variability, ranging from approximate to fairly precise, depending on the type of design used.

The basis of Design of Experiments (DOE) is statistics. The goals of that science are to develop the best methods for generating data (referred to as sampling techniques), and then to use mathematical methods to extract as much information as possible from data, while also estimating the comparative validity of any conclusions drawn from the analysis. Depending on the amount and quality of data, conclusions may be reached with a wide range of confidence; sometimes very little (low probability of being correct) to high confidence (probability range of 90–99 percent of being correct).

DOE methods are mainly about sampling techniques; that is, what series of related experiments (referred to as runs or treatments) will generate information about the process most efficiently. Each design (which is referred to in the singular) is actually a set of experimental runs. There are numerous families of designs from which the experimenter can choose, depending on the process under investigation, the number and kind of factors that are known or believed to affect its output, and what kind of information the experimenter desires to obtain. Designs can contain as few as four runs, and as many as 256 or more, but the majority of them in common use fall in the range of 8 to perhaps 32.

One might think of the collection of designs as a toolbox that contains sets of various types of tools, screwdrivers, chisels, wrenches, and so on. The different types of designs are like the different families of tools, made to be applied to different tasks. Some design types are basic and not difficult to understand, others are more advanced and more challenging for the plastics technologist. One should keep in mind the words of Nobel Laureate William Lipscomb, “Difficult merely means one hasn’t seen it before.”

22.2 APPLICATION OF DOE

The application of DOE starts with a careful examination of the process, leading to a listing of the factors that may affect it, and what range of each factor is likely to affect the process. For instance, if a polymerization process were being investigated, the factors of monomer concentration, catalyst type, catalyst concentration, temperature, time, reaction vessel size, and agitation rate might be considered.

The experimenter (or the team) might decide to concentrate on an available reaction vessel size, a standard agitation rate, and a time that should be ample for the reaction to reach completion. Then they would have to rely on experience or literature search to help select the extent to which each factor should be changed in the experiment. If they were not ready for more advanced optimization designs, they could easily choose either of the examples shown in Tables 22.1 and 22.2 to begin exploring the process.

A factorial experiment, by definition, is one consisting of two or more variable factors, whose assigned values are usually called levels. The term appears to have been coined by Ronald Fisher in 1926. If all possible combinations are used, the experiment is referred to as full factorial. Very commonly, half of the possible combinations are used; the experiment then designated as half-factorial. Example 1 uses the half-factorial design.

Each row in these examples is an individual experiment (also referred to as a run or treatment), which sets the conditions to be used once in the series shown. For each run there will be a response; in this case, it would likely be the percentage conversion, but usually there can be several results measured for a process. For instance, average

TABLE 22.1 Example 1

Run #	Monomer Concentration	Catalyst	Catalyst Concentration	Temperature (°C)
1	60	Pt	0.2	120
2	60	Pt	0.1	100
3	60	Ni	0.2	100
4	60	Ni	0.1	120
5	40	Pt	0.2	100
6	40	Pt	0.1	120
7	40	Ni	0.2	120
8	40	Ni	0.1	100

molecular weight, degree of branching, and viscosity of the final product could also be useful responses. Each type of response would be analyzed using statistical methods to see how it was affected by the factors, and a mathematical model of the relationship between the response and the factors would be derived. The model will predict how to change the factors to control the process, and the precision of its predictions will depend on how well the experiment turned out. With the more advanced designs and rigorous implementation of the experiment, the predictions can be very good.

Both Examples 1 and 2 have the same ranges used for the factors of monomer concentration, catalyst concentration, and temperature. Example 2 has both catalyst types used in Example 1, plus one new one, and one more run than Example 1. Thus, these different patterns of experimental runs would seem to be closely related. What are the differences between them?

Example 1 is a two-level factorial design, with two levels of catalyst concentration, and is half-factorial; that is, half of the possible combinations are omitted in a systematic manner. It can only show linear contrasts as the level of each factor is changed. It will allow calculation of main factor effects cleanly, but possible interactions will be confused with each other mathematically (referred to "aliasing"). Sometimes, with half-factorials the interactions can still be extracted and understood.

TABLE 22.2 Example 2

Run #	Monomer Concentration	Catalyst	Catalyst Concentration	Temperature (°C)
1	60	Pt	0.2	120
2	60	Ag	0.15	110
3	60	Ni	0.1	100
4	50	Pt	0.15	100
5	50	Ag	0.1	120
6	50	Ni	0.2	110
7	40	Pt	0.1	110
8	40	Ag	0.2	100
9	40	Ni	0.15	120

Example 2, which uses four factors at three levels, is from a family of multi-level designs formally known as hyper-Graeco-Latin squares. A Latin square is an $n \times n$ square grid filled with symbols (letters or numbers) so that each symbol appears once and only once in each row or column. When $n = 9$ and the symbols are numbers, the result is the familiar Sudoku puzzle. The concept appears to have been devised by Arabic mathematicians in the Middle Ages. The simplest $n = 3$ is

$$\begin{array}{ccc} \mathrm{A} & \mathrm{B} & \mathrm{C} \\ \mathrm{B} & \mathrm{C} & \mathrm{A} \\ \mathrm{C} & \mathrm{A} & \mathrm{B} \end{array}$$

It has been demonstrated that Latin squares can be constructed where $n = 3$ to 10, except for $n = 6$. If symbol pairs are used, typically combinations of one Latin and one Greek letter, the result is called a Graeco-Latin or Euler square, for Leonhard Euler, the Swiss mathematician, who demonstrated their utility in the 1780s. The $n = 3$ Graeco-Latin Square is then

$$\begin{array}{ccc} \mathrm{A}\alpha & \mathrm{B}\gamma & \mathrm{C}\beta \\ \mathrm{B}\beta & \mathrm{C}\alpha & \mathrm{A}\gamma \\ \mathrm{C}\gamma & \mathrm{A}\beta & \mathrm{B}\alpha \end{array}$$

It can be seen that both the Greek and Latin characters form Latin squares. Every Graeco-Latin square consists of two Latin squares that are orthogonal, that is, that every pair occurs exactly once. (Graeco-Latin alphanumeric Sudoku puzzles have appeared, but are not as yet popular.) In general, there are $n-1$ solutions; above, where $n = 3$, one has the A, B, C and the α, β, γ sets. With $n = 4$, there are three solutions:

$$\begin{array}{cccc} \mathrm{A} & \mathrm{D} & \mathrm{B} & \mathrm{C} \\ \mathrm{D} & \mathrm{A} & \mathrm{C} & \mathrm{B} \\ \mathrm{B} & \mathrm{C} & \mathrm{A} & \mathrm{D} \\ \mathrm{C} & \mathrm{B} & \mathrm{D} & \mathrm{A} \end{array} \qquad \begin{array}{cccc} \mathrm{A} & \mathrm{D} & \mathrm{B} & \mathrm{C} \\ \mathrm{C} & \mathrm{B} & \mathrm{D} & \mathrm{A} \\ \mathrm{D} & \mathrm{A} & \mathrm{C} & \mathrm{B} \\ \mathrm{B} & \mathrm{C} & \mathrm{A} & \mathrm{D} \end{array} \qquad \begin{array}{cccc} \mathrm{A} & \mathrm{D} & \mathrm{B} & \mathrm{C} \\ \mathrm{B} & \mathrm{C} & \mathrm{A} & \mathrm{D} \\ \mathrm{C} & \mathrm{B} & \mathrm{D} & \mathrm{A} \\ \mathrm{D} & \mathrm{A} & \mathrm{C} & \mathrm{B} \end{array}$$

The more than three-dimensional designs are referred to as hyper-Graeco-Latin squares, or a complete set of mutually orthogonal Latin squares. In Example 2, the use of four factors at three levels adds the prefix "hyper."

The $n = 3$ hyper-Graeco-Latin square is often referred to as a Taguchi L9, after Genichi Taguchi, the Japanese engineer who famously explored the cost to society of manufacturing defects. In Example 2, it is really a screening design that displays contrasts between categorical factors (such as catalyst type) and has the capacity to show nonlinear effects of numerical factors. It unfortunately aliases all interactions that may exist in the process, so they cannot be understood.

In this particular case, the experimenter would not be likely to use the first design, from realization that the factors could (and probably do) interact. Thus, while the design of Example 1 would increase understanding of the process somewhat, it would leave critical questions about interactions unanswered. Example 2 might be chosen as a quick and easy way to sort out the possible catalyst types and get a good idea of how linear or nonlinear the effects of the numerical factors might be. It would still be a flawed design, because of the certainty that important interactions exist and would remain undetected.

The knowledgeable experimenter would more likely go to a two-level full-factorial design of 16 runs, which allows for complete analysis of interactions. Other possibilities also exist; in DOE, it is often true that there is "more than one way to skin a cat." (The maxim was considered old in 1678, and may or may not relate to the furrier's trade.)

Using DOE requires a mental adjustment for many scientists and engineers, since the methods require more preliminary work. The habit of thinking in terms of 8, 12, 16, or more runs may take time and experience. The traditional approach is to consider running very few experiments, perhaps 2 or 3, often based on more or less relevant experience or intuition, or even convenience. In fairness, once in a while, by luck or inspiration, such empirical methods succeed. The systematic approach of using designed experiments is enormously more powerful in the long run. The efficiency of using designs is undeniable. It corresponds to the old carpenter's rule—*Measure Twice, Cut Once* (attributed to Posidonius, 135–51 BCE, whose philosophical writings were thought to cover every subject imaginable). Preparing to do something carefully and methodically is the professional and most efficient way.

The real benefits of DOE practice can be summed up in what the author has called Del Vecchio's Rule:

> **A properly designed and implemented experiment will always yield important information.**

One must note that, following Pasteur, the mind of the experimenter must be prepared to appreciate the importance. A corollary is that practice of DOE will add to preparation.

Conclusions from the examples are likely to fit into categories such as how to use process parameters to optimize output (a common industrial goal); or that the factors and levels chosen will not provide the desired output in any combination (not exactly what was hoped for, but a critical bit of information in design of further experiments); or that factors other than the ones used must have major influence on the process (again, not the goal, but important); or that the measurement system used is not sensitive or reliable enough to detect accurately and precisely the changes in output produced (also of great importance).

The advantage of reaching conclusions of guaranteed significance is compelling. The technologist who does not investigate DOE methods is denying himself or herself a great opportunity to acquire a powerful tool for problem solving as well as the satisfaction and enjoyment of pursuing meaningful programs.

22.3 HOW TO START

Once a person or organization is ready to commit to DOE methods, there are several ways to go about acquiring the basic skills. First, of course, is to take a course on the subject. These are offered by the mathematics departments of some universities as a subset of statistics. Most of the time there are prerequisite courses in basic statistics. Very often, such university courses are taught by statisticians and targeted for fledgling statisticians, which means they tend to be heavy in theory and advanced mathematical techniques.

More often in industry, people will make use of continuing education courses from professional organizations, or independent instructors who teach an in-house course. (For groups of any size, this is almost always the most cost-effective way to promote the acquisition of skills.) There are many books on the subject, but most are not easy reading and fail to take the reader into step-by-step practice.

Lastly, sometimes a company will invest in software, and rely either on the accompanying manuals, or on a course offered by the software company, to bring their employees up to basic skill levels. There is a danger in overestimating the ability of a software package to lead anyone into really good use of DOE. Just as buying a word processing program will not make anyone a professional writer, neither does having a powerful DOE software package guarantee that the best designs for given problems will be used. The human element in choosing factors and levels to be varied, and the particular pattern of experiments to apply, are absolutely critical.

It is quite possible to use many designs with pencil and paper (as was done for close to 100 years), or enter the designs into a computer spreadsheet and apply and analyze them more easily that way. With the advent of computers and software to make everything enormously more convenient, very few practitioners do anything without the benefit of their favorite statistics program.

There are two kinds of programs that help the experimenter formulate and analyze designed experiments. The first kind are the major statistics software packages, such as JMP® (SAS Institute) and Statistica® (StatSoft), which contain many kinds of statistical tools in different modules, one of which is DOE. These are general purpose programs of very broad applicability, often used by company statisticians. They can also be used by nonspecialists, but can be challenging to learn. For companies that will make use of many of their modules, they are effort-efficient.

The second type of program is the specialized DOE variety such as DesignExpert® (Stat-Ease) and E-Chip (Echip, Inc.), which address designed experiments only. These tend to be more user-friendly, and may cost less to purchase and maintain.

No program will make drawing up an experimental design an automatic process. When the user has selected the process control factors to be varied, and how to vary them, software will then make it easy to sort through possible designs that can utilize that number and type of factors. The final choice of a design is still up to the experimenter. Sometimes, the situation will lead to a single obvious design; at others, there could be several ways to proceed using different designs, and only the human mind will be able to weigh the alternatives and make the final decision.

When the design has been chosen and the experiments run, the results are entered into the software, and the second major convenience of software emerges. Statistical routines are applied to the data with very little effort on the part of the experimenter. The analysis can then be examined in several different ways, starting with a table of results, but also by means of numerous graphical methods. These are often quite helpful in making clear what the data demonstrate. The charts and graphs from current programs can be copied and imported into reports and presentations—a very advantageous feature in today's graphics-oriented business practice.

22.4 THE CRITICAL STEPS

The effectiveness of an experiment hinges completely on the choices the experimenter makes about which elements of the process to choose and how they will be varied in attempting to explore the process. This applies to designed experiments at least as strongly as to any other way of proceeding. How, then, does one make these essential selections before starting the software?

The first step is to begin with a blank slate view of the process. For complex processes, it is essential to assemble a team of people who are or have been involved in elements of the process. Often, background knowledge of a process by those most familiar with how it (or a previous version) has run in the past is invaluable in developing the experimental plan.

A careful listing of all possible independent process variables is made, sometimes in a group "brainstorm" session. Even comparatively minor or questionable contributing factors are included. Once this has been accomplished, the discussion moves on to which of them are most likely to be most significant, and after that, how easily they might be controlled in an experiment. (Sometimes, a variable will certainly have the potential to be very important, but will be difficult to vary easily in an experiment; for instance, changing the operating temperature of a very large piece of equipment that takes a long time to reach thermal equilibrium.)

In this part of the process, some factors may be dismissed as trivial, others may be deemed important but may not be part of the initial experiment, for example, because of difficulty in obtaining a range of input. When the final list of candidate factors has been agreed upon, each is then examined to determine what range of levels should be used. These are matters such as upper and lower temperatures, pressures, or ingredient concentrations (continuous variables) and choice of catalysts, mixing procedure, or source of raw material (discrete or category variables). Depending on prior knowledge or research, a factor might be varied narrowly or more broadly. For one process the temperature might vary $\pm 20\,^{\circ}\mathrm{C}$, for another, only $\pm 5\,^{\circ}\mathrm{C}$.

Once these essential preliminary steps have been taken, the experimenter (or the team) begins to look at possible designs that might apply, and how practical it will be to implement a given design in their particular circumstance. Experiments that can be performed in the laboratory on a small scale are often feasible even if involving a substantial number of runs. In factory situations, restrictions in time, equipment, or production schedules may make it difficult or impossible to use a design with a high number of runs. Such considerations may force the experimenter to re-examine the design options and go to a simpler and smaller design, or an incremental series of small designs. It is much better to run a smaller design that can be performed with good controls than to attempt a larger, more advanced design that will be very risky in implementation. If the experiments can be miniaturized and perhaps run automatically, the designed procedure is sometimes referred to as high-throughput experimentation. It is valuable in situations where the underlying mechanisms are poorly understood, as with development of pharmaceuticals.

When the decisions have been made, and the set of runs have been laid out (randomized by the software), the final challenge must be met. That is to make everything happen according to plan, with as much precision as can possibly be attained. This seems simple enough, but often the reality of getting every i dotted and t crossed is much more complex and difficult. Since the quality of the analysis depends directly on the quality of generated test data, and the scatter in the test data is a direct function of the precision with which the experimental runs are performed, a poorly implemented design will provide impaired analyses, and understanding of the process results will not be optimal. In the worst case, the experiment can prove useless. Therefore, a careful plan for running the experiment, with close attention to detail during its execution, is essential.

22.5 ANALYSIS OF THE DATA

Once again, the convenience of computer software comes into play. The statistical technique is called analysis of variance (ANOVA). In this method, the variation among the results is examined to determine what relationships there are between the process control factors and the process output. Many possible relationships exist; for a process with four main factors, there are actually 15 possible ways in which the process might respond to changes in the control factors.

Table 22.3 shows a four-factor experiment, of the family of two-level full factorial designs. The process is a polymerization, with the amount of monomer, the reaction temperature, the reaction vessel pressure, and the amount of catalyst as the independent variables. The yield of polymer is the response or dependent variable.

A quick look at the response column reveals that the yield has ranged from 50 to 90 percent, which demonstrates that these factors do indeed affect the process. The question then becomes, how do they affect it, exactly? The answer is in the ANOVA table (Table 22.4).

There is a great deal of information contained in this table, but only the most critical parts will be discussed here. On line 2, the last cell contains "<0.0001," and this indicates that the probability of the derived model for the process being valid is above 99.9 percent. In other words, the experiment was highly successful in finding a way to describe how the control factors affect the process output.

On line 11, the "R-squared" term is indicated to be 0.9933. This tells the experimenter that over 99 percent of the pattern of variation in all the 16 results is explained

TABLE 22.3 Four-Factor Experiment

Run	Reactor Load (kg)	Temperature (°C)	Pressure (atm)	Catalyst (%)	*Conversion* (*Yield*) (%)
1	100	180	1	2	*71*
2	125	180	1	2	*61*
3	100	180	10	2	*68*
4	125	180	10	2	*61*
5	100	200	1	2	*90*
6	125	200	1	2	*82*
7	100	200	10	2	*87*
8	125	200	10	2	*80*
9	100	180	1	3	*61*
10	125	180	1	3	*50*
11	100	180	10	3	*59*
12	125	180	10	3	*51*
13	100	200	1	3	*89*
14	125	200	1	3	*83*
15	100	200	10	3	*85*
16	125	200	10	3	*78*

by the derived model. Line 2 indicated the model was valid; line 11 demonstrates how accurate it is.

Lines 18–22 tell the experimenter about the derived model. The numbers lined up with each factor indicate how much that factor affects the process as compared to the others. For instance, the reactor load has a coefficient of 4, while temperature has a coefficient of 12. This means that, for the ranges of change each one of those factors had in the experiment, temperature had three times as much effect as reactor load did.

Line 22 is of special interest, because it is not any of the individual factors, but is shown as "BD," which means that describes an interaction between factor B, temperature, and factor D, catalyst concentration. In this case, other significant interactions did not surface. Other features of the software can be used to display facets of the process, and a graphical illustration of the BD interaction is shown in Fig. 22.1.

This figure demonstrates the nonparallel effects of temperature and catalyst concentration. At the lower temperature, the amount of catalyst has an effect on the yield; but at the higher temperature, the yield is increased overall and there is no longer any detectable effect of catalyst concentration. The directions suggested for further experimentation are obvious.

Modern DOE software comes with a wide array of graphics features, including color coding and 3-D representations, among others. Also, the data in the file can be exported to, or imported from, common spreadsheet formats, which can also be quite convenient.

One of the most useful features is an optimization subroutine. When a process has several responses to be measured (e.g., tensile strength, modulus, stress relaxation, resistance to heat/fluids, and flex life), the analysis of each response will result in

TABLE 22.4 ANOVA for Selected Factorial Model: Analysis of Variance Table (Partial Sum of Squares—Type III)

1	Source	Sum of Squares	df	Mean Square	F-value	p-value, Prob > F
2	Model	2782.25	5	556.45	296.77	<0.0001
3	A: Reactor Load	256.00	1	256.00	136.53	<0.0001
4	B: Temperature	2304.00	1	2304.00	1228.80	<0.0001
5	C: Pressure	20.25	1	20.25	10.80	0.0082
6	D: Catalyst	121.00	1	121.00	64.53	<0.0001
7	BD	81.00	1	81.00	43.20	<0.0001
8	Residual	18.75	10	1.88		
9	Cor. Total	2801.00	15			
10						
11	Std. Dev.	1.37	R-Squared	0.9933		
12	Mean	72.25	Adj. R-Squared	0.9900		
13	C.V. %	1.90	Pred R-Squared	0.9829		
14						
15	Coefficient	Standard	95% CI	95% CI		
16	Factor	Estimate	df	Error	Low	High
17	Intercept	72.25	1	0.34	71.49	73.01
18	A: Reactor Load	−4.00	1	0.34	−4.76	−3.24
19	B: Temperature	12.00	1	0.34	11.24	12.76
20	C: Pressure	−1.13	1	0.34	−1.89	−0.36
21	D: Catalyst	−2.75	1	0.34	−3.51	−1.99
22	BD	2.25	1	0.34	1.49	3.01

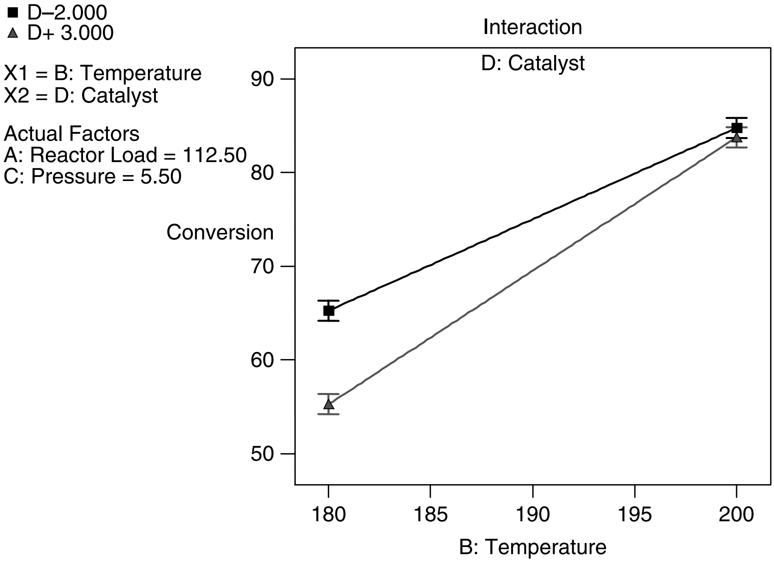

Figure 22.1 Illustration of the BD: interaction for the experiment described in Tables 22.3 and 22.4.

a model describing that response. The optimization feature can run a complex series of operations, using all the models at once, to predict process outcomes as the factors are varied. The user can list desired levels of each response, and the optimization routine will seek the combination of factors that can provide all of the desired responses. If this proves to be impossible, the program will still help the user find the optimum combination. For complex processes with a variety of responses, this feature is really invaluable to the experimenter.

22.6 DOE—WHY NOT?

The question arises as to why more scientists and technologists do not try to acquire skill in DOE, particularly when computer software makes its use so much easier. Those who have taken the time and made the effort are always enthusiastic about the benefits to be had, and many say they only wish they had learned DOE years earlier.

The most common reason given for not exploring DOE is lack of time, and the second, that it is something new, a change, and one that people think will involve having to learn and use higher mathematical techniques. The latter is no longer true, and the former is one of those reasonable but ultimately weak rationalizations for not doing something that really should be done.

There is much emphasis today on process optimization and widespread use of schools of thought such as the Six Sigma™ program (a set of practices originally developed by Motorola in 1986 to improve processes by reducing defects to a level of less than 3.4 per one million opportunities). In consequence, DOE has become a basic tool that no practicing technologist should ignore. In the example above, the discovery of a reaction temperature/catalyst level interaction would prove invaluable to optimization of the process. In order for this to be found by empirical experiments without organized design, barring accidental discovery, one would have to understand the mechanism involved in the process on a molecular basis (i.e., already know the answer). Neither is usually the case. On the contrary, the results of designed experiments are likely to lead to an understanding of underlying mechanism or to a decision regarding competing theories.

The benefits of DOE are more than technological. Consider the polymerization of isobutylene. The conclusion that it must be carried out at extremely low temperatures to produce highly useful products is not what management had been hoping for. A proposal for installation of massive cooling capacity has greater likelihood of approval when documented by thoroughly analyzed results of designed experiments. The establishment of a DOE program is also a prerequisite for the development of on-line data acquisition meaningful for use in automated control systems. In this area, it has been in use in instrument design for some time. The application to formulation is more recent, but certainly just as promising.

ADDITIONAL READING

1. R. J. Del Vecchio, *Understanding Design of Experiments*. Hanser, 1997.

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Handbook of Vinyl Formulating, Second Edition. Edited by Richard F. Grossman