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Woodhead Publishing Series in Textiles: Number 116

# Handbook of textile and industrial dyeing

Volume 1: Principles, processes and  
types of dyes

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Edited by  
M. Clark



Oxford    Cambridge    Philadelphia    New Delhi

Published by Woodhead Publishing Limited,  
80 High Street, Sawston, Cambridge CB22 3HJ, UK  
www.woodheadpublishing.com

Woodhead Publishing, 1518 Walnut Street, Suite 1100, Philadelphia,  
PA 19102-3406, USA

Woodhead Publishing India Private Limited, G-2, Vardaan House, 7/28 Ansari Road,  
Daryaganj, New Delhi – 110002, India  
www.woodheadpublishingindia.com

First published 2011, Woodhead Publishing Limited  
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British Library Cataloguing in Publication Data  
A catalogue record for this book is available from the British Library.

Library of Congress Control Number: 2011935501

ISBN 978-1-84569-695-5 (print)  
ISBN 978-0-85709-397-4 (online)  
ISSN 2042-0803 Woodhead Publishing Series in Textiles (print)  
ISSN 2042-0811 Woodhead Publishing Series in Textiles (online)

The publisher's policy is to use permanent paper from mills that operate a sustainable forestry policy, and which has been manufactured from pulp which is processed using acid-free and elemental chlorine-free practices. Furthermore, the publisher ensures that the text paper and cover board used have met acceptable environmental accreditation standards.

Typeset by Newgen Publishing and Data Services  
Printed by TJI Digital, Padstow, Cornwall, UK



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## 1.1 Introduction

The human race has been interested in colouring materials since prehistoric times typified by the application of natural dyes for furs and textiles. These early dyes were mainly of vegetable origin, with some also of animal origin. Developments extending over many thousands of years led to rather complicated dyeing processes being produced. Among these were *woad* (natural indigo) which was obtained from the plant *Indigofera tinctoria*, Tyrian purple which was extracted from the gland of a purple snail and developed by the Phoenicians and Alizarine which was obtained from madder Campeachi wood extract.

The use of picric acid, obtained by Wolfe in 1771 by treating indigo with nitric acid, was subsequently used for dyeing silk yellow, but did not gain any significant attention. In 1856, William H. Perkin succeeded in obtaining a dye he called *Mauvine*. This was achieved by oxidation of a mixture of aniline bases to produce a violet cationic dye. The brilliant violet hue on silk attracted immediate attention and stimulated other chemists to carry out similar experiments. In this way similar discoveries were achieved; in 1859 Verguin discovered *fuchsine*, while Griess discovered diazo compounds which led to the development of the currently large class of synthetic dyes, namely the azo compounds. The first true azo dye, Bismark Brown, was developed by Martius in 1863.<sup>1</sup>

This chapter discusses the principles of dyeing in a general manner, the classification of dyes highlighting specific examples of dye classes. The following chapters will present considerably more detailed discussions regarding textile and industrial dyeing with reference to principles, processes and types of dyes.

## 1.2 Principles of dyeing

The objective of dyeing is to produce uniform colouration of a substrate usually to match a pre-selected colour. The colour should be uniform throughout the substrate and be of a solid shade with no unlevelness or change in shade over the whole substrate. There are many factors that will influence

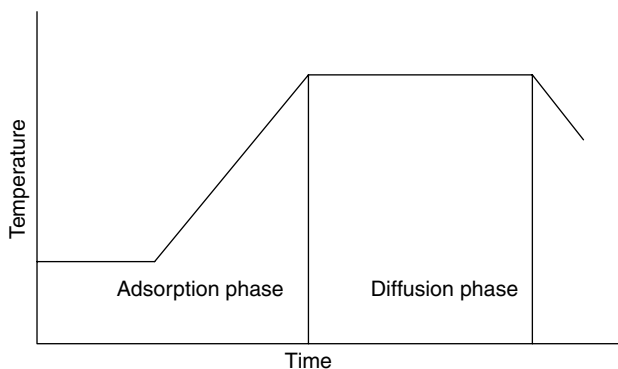
the appearance of the final shade, including: texture of the substrate, construction of the substrate (both chemical and physical), pre-treatments applied to the substrate prior to dyeing and post-treatments applied after the dyeing process. The application of colour can be achieved by a number of methods, but the most common three methods are exhaust dyeing (batch), continuous (padding) and printing.

### 1.3 Exhaust dyeing

In exhaust dyeing the dye, which is wholly or partially soluble in the dye-bath, is transported to the fibre surface by the motion of the dye liquor or by motion of the substrate being dyed. The dye is adsorbed onto the fibre surface and ideally diffuses into the whole of the fibre. Depending upon the dye being used, the interactions between the dye and the fibre can be either chemical or physical. Exhaust dyeing is usually conducted using dilute solutions of dyes, normally termed long liquor dyeing, and can involve liquor to substrate ratios from 8:1 up to 30:1. As described above there are two main phases to exhaust dyeing, the adsorption phase and the diffusion phase. Most exhaust dyeing involves a temperature gradient whereby the dyeing is commenced at a fairly ambient temperature (30–40°C) with the temperature being increased slowly up to a final temperature which is dependent upon the dyes being used (Fig. 1.1).

Depending upon the dyes being used, during the diffusion phase, changes to the dyebath pH may be made to facilitate covalent fixation of the dye which has diffused into the substrate.

Exhaust dyeing recipes, including auxiliaries together with the dyes, are traditionally made up by percent weight relative to the weight of substrate being dyed. The auxiliaries are introduced first into the dyebath and allowed to circulate to enable uniform concentration throughout the dyebath and



1.1 Typical dyeing profile.

on the substrate surface. The dyes are then introduced into the dyebath and again allowed to circulate before the temperature is raised in order to obtain a uniform concentration throughout the dyebath. Gaining uniform concentrations of both auxiliaries and dyes is paramount since non-uniform concentrations on the substrate surface can lead to unlevel dye uptake. The speed of dye uptake (exhaustion) of individual dyes can vary and will depend upon their chemical and physical properties together with the type and construction of substrate being dyed. The dyeing rate also depends upon the dye concentration, the liquor ratio, temperature of the dyebath and the influence of the dyeing auxiliaries. Rapid exhaustion rates lead to unlevelness of dye distribution over the substrate surface, so dyes have to be carefully selected when used in multi-dye recipes; many dye manufacturers produce information stating which dyes from their ranges are compatible to achieve level build-up of dye during dyeing. Dyers wish to achieve the highest exhaustion possible to minimise dye remaining in the effluent and increase batch to batch reproducibility, whilst still obtaining the shade required by the customer. The dyeing process will eventually end in equilibrium, whereby the dye concentration in the fibre and the dyebath do not change significantly. It is envisaged that dye adsorbed onto the substrate surface has diffused into the whole of the substrate resulting in a uniform shade required by the customer and that there is only a small concentration of dye left in the dyebath. This is where the final shade of the substrate is checked against the standard. If there is any deviation from the required shade, small additions of dye may be made to the dyebath to achieve the required shade.

Dyers wish to achieve the correct shade the first time of dyeing in order to minimise further processing and reduce costs. In order to do this uniform dyeing rates and high exhaustion rates of dyes are required. To achieve short dyeing cycles, thereby maximising production, most modern dyeing equipment is enclosed ensuring that the dyebath is maintained at the required temperature and that there are no temperature variations within the dyebath. Some dyeing machines can be pressurised enabling the dye liquor to be heated to 130°C allowing substrates, such as polyester, to be dyed without the requirement of carriers.

There are two types of machinery available for exhaust dyeing: circulating machines whereby the substrate is stationary and the dye liquor is circulated, and circulating-goods machines in which the substrate and the dye liquor are circulated.

### 1.3.1 Circulating machines

The substrate, in the form of loose stock, sliver, tow, yarn or fabric, is packed into canisters, wound onto cones or perforated beams and placed inside the

dyeing vessel. The dye liquor is pumped through the substrate in two directions, in to out and out to in so that all the substrate has uniform contact with the dye liquor. Pump speeds can be varied to obtain a range of liquor flow rates, since the density of the compacted material will influence the liquor flow rate. Evenness of packing is crucial in obtaining levelness throughout the substrate. Inconsistencies in packing may lead to channelling of the dye liquor which would result in some parts of the substrate being dyed to a greater depth than other areas.

### 1.3.2 Circulating-goods machines

Some hank dyeing machines and particularly fabric dyeing machines fall into this category of dyeing machine. Fabric dyeing was traditionally carried out on a winch, whereby the fabric was drawn in rope form through the dyebath via a driven winch reel, the speed of which could be adjusted depending on the fabric length and construction. However, these have been largely superseded by pressurised jet dyeing machines. These machines circulate both the fabric, via a winch reel, and the dyebath via the jet. The dyebath is 'injected' into the fabric as it passes through the jet nozzle. Jet dyeing machines are capable of running at very low liquor ratios, typically 8:1, although some may run as low as 4:1, enabling savings in water and energy to be made by the dyer. Jiggers were also commonplace with winch machines, where the fabric is mounted in whole width on a beam and guided back and forth through the dyebath in open width.

## 1.4 Continuous dyeing

Continuous dyeing is a process whereby dyeing the fabric and fixation of the dye are carried out continuously in one simultaneous operation. This is traditionally accomplished using a production line system where units are assembled into lines of consecutive processing steps; this can include both pre- and post-dyeing treatments. Fabric is usually processed in open width, so care must be taken not to stretch the fabric. The fabric running speed dictates the dwell time of the fabric through each treatment unit, although dwell times can be increased by using 'festoon' type fabric transport. The main disadvantage to continuous processing is that any machinery breakdown can cause ruined fabric due to excessive dwell times in specific units whilst the breakdown is being rectified; this can be a particular problem when stenters running at high temperatures are employed since fabrics may be severely discoloured or burnt.

The application of dye can be conducted either by direct application, whereby the dye liquor is sprayed or printed onto the substrate, or

by continuous immersion of the fabric in a dyebath and excess dye liquor removed by squeeze rollers (padding).

Padding involves passing the substrate through a pad trough containing the dye liquor. It is imperative that the substrate is wet out thoroughly as it passes into the dye liquor to minimise unlevelness. The amount of dye liquor retained by the substrate after squeezing is governed by the pressure of the squeeze rollers and substrate construction. The amount of liquor retained is termed 'pick up', a low pick up being preferable since this minimises migration of dye liquor in the substrate and saves energy during drying.

In order to obtain a uniform fixation of dyes on the substrate, it is preferable to dry the fabric after padding and before it passes on to the next process. Drying equipment is normally infrared heat or by hot air stream and should be contact-free to avoid marking of the substrate and soiling of the drying equipment.

After drying, the dye is only deposited on the surface of the substrate, it must penetrate into the substrate during the fixation step and become part of the substrate via chemical reaction (reactive dyes), aggregation (vat and sulphur dyes), ionic interaction (acid and basic dyes) or solid solution (disperse dyes). Fixation is performed under a number of conditions depending upon the dye and substrate involved. Generally saturated steam at 100°C is used for the majority of dyes. Disperse dyes are fixed in polyester substrates by the Thermasol Process whereby the substrate is heated to at 210°C for 30–60 s in order for the dyes to diffuse into the substrate. After fixation substrates are usually washed to remove unfixed dye and auxiliaries.

## 1.5 Printing

There are a wide number of methods for applying dyes by printing techniques. The most common method is direct printing whereby the dyes are applied in the form of a print paste containing thickeners and auxiliaries. The print paste is applied to the fabric via a roller, in the case of engraved cylinders, or by screens in the case of flat or rotary screen printing. Following printing the prints are dried and steamed similar to the processes used for padding, depending upon the dyes being printed. Each colour of the design requires its own screen so printing machines can take up a significant amount of space, especially a flat screen machine. Pigment printing involves the use of binders to adhere the pigment to the substrate surface. Pigment prints usually only require drying/curing after the printing process.

Ink-jet printing is rapidly becoming a popular method of producing patterned designs on fabrics. Production speeds are not as fast as rotary screen printing, with machines running at 20–30 m/min depending on the complexity of the design being printed. Ink-jet printing poses no problems with soluble dyes for printing substrates such as cotton, nylon, wool, etc., but disperse

dyes and pigments must be finely dispersed within the printing ink to avoid blocking of the ink-jet nozzles which can be costly to replace and time consuming to unblock.

## 1.6 Classification systems for dyes

Dyes may be classified according to many parameters, such as chemical structure, colour, application, fastness, manufacturer, synthesis route, date invented, to name only a few. In order for us to construct a classification system we must first ask the question ‘Who would use a classification system for colourants?’ The answer to this question could encompass many users including: the textile industry, paint and ink manufacturers, artists and designers, dye and pigment manufacturers, students and researchers, so we can see that there is a need for a classification system for both dye producers and dye users, but such a system must allow an unambiguous dialogue between user and producer for such a classification system to be successful. Table 1.1 highlights some of the reasons why both a producer and user would want to classify dyes.

Nowadays when we think of classification of dyes we automatically think of the *Colour Index* published by the Society of Dyers and Colourists, but this was not the first attempt at classifying dyes. Following the synthesis of Mauvine by Perkin in 1856, many other workers were encouraged to produce new synthetic colourants. Although the first synthetic dyes were produced in the UK there was a distinct shift of production to Germany in the late nineteenth century. The first book to provide comprehensive information regarding dyes and pigments used within the colouration industry was *The Manual of Colours and Dyewares* by J. W. Slater, published in 1870 with a second enlarged edition being published in 1882.<sup>2</sup> The colourants (both natural and synthetic) were listed alphabetically together with chemicals used within the colouration process. Slater states in the preface of his publication that he intends to provide the reader with ‘an account of chemical products and natural wares used in dyeing, printing and accessory arts’.

*Table 1.1* Reasons for classification of dyes

Producer	User
Chemical structures	Distinguish between products
Preparation methods	Find manufacturers
Information on properties and uses	Information on properties and use
Competitor products	Health and safety information for employees
Aid health and safety	Environmental legislation compliance
Environmental legislation compliance	



He also acknowledges that, since the recent growth of synthetic colourants, such a publication of the 'tinctorial art' will 'render older authorities defective and in some measure obsolete'.

Since the dye manufacturing industry was growing in Germany a further attempt at dye and pigment classification was published in 1883 by R. Benedikt, *Die Künstlichen Farbstoffe (Theerfarben) (Synthetic Dyes (Coal-Tar Products))*, an English translation of which appeared in 1886 under the title *The Chemistry of Coal-Tar Products* by R. Benedikt and E. Knecht and was followed by a second edition in 1888 which encompassed sections of 'Tabellarische Übersicht der Künstlichen Organischen Farbstoffe' ('Tabular Survey of Synthetic Organic Colouring Matters') by G. Schultz and P. Julius.

In the books by Benedikt and Knecht, dyes were classified by structure and group classification within each structure was by hue in spectral order. Since there was a lack of books in English, the *Dictionary of Coal Tar Colours* was produced by G. H. Hurst and published in 1882 with a second enlarged edition in 1896. These later books started to classify dyes and pigments in order of commercial name, name of manufacturer, formula (where known), name of discoverer, properties and uses. This same alphabetical order was used by W. M. Gardner and W. F. Laycock in their book *A Dictionary of Dyes, Mordants and Other Compounds used in the Dyeing and Calico Printing*, published in 1901 and reprinted in 1905 and 1918, revised in 1926.

In 1914 the outbreak of World War One led to links with the German industry being cut and so there was a need for an English-language classification system for colourants, since from 1888 to 1914 the number of synthetic colourants had risen from 278 to 1001. The fifth edition (1914) of the book by Schultz and Julius was considered out of date due to significant changes within the colour industry and the rapid expansion of new colourants. In 1921 the Society of Dyers and Colourists started the production of a 'Colour Index' to fulfil the need for a book which would provide concise information regarding the constitution and properties of the whole range of colours used in dyeing, printing and paint industries. Dr F. M. Rowe, who became Professor of Colour Chemistry and Dyeing in the University of Leeds in 1926, was appointed the editor of this first *Colour Index*. The first publication was scheduled for 1921, but there were significant delays due to the Society being overwhelmed with information from manufacturers and also the Society wanted all the information to be accurate, so it was decided to trace back to original sources every reference to patents and publications in the scientific and technical literature for verification. The first twelve parts of the *Colour Index* were issued in September 1922 with subsequent parts being issued monthly. The work was completed by the end of 1923 and bound copies of the *Colour Index* were available in

January 1924. The colourants were divided into three groups: 1. Synthetic Organic dyes (1–1230), 2. Natural Organic Dyes (1231–1254) and 3. Natural and Synthetic Inorganic Colouring Matters (1255–1316). The information on each colourant was arranged in the following manner:

- Index numbers (together with the Schultz number from the fifth and sixth editions of *Farbstofftabellen*)
- Commercial name and manufacturer
- Scientific name/components/formula
- Preparation
- Discoverer/literature citations
- Description/properties/mode of application (including fastness properties and in some cases absorption spectra).

Rowe and his committee believed that 50 years hence the book would be the standard work on the subject. Little did they realise the extent to which their prophecy would be fulfilled.

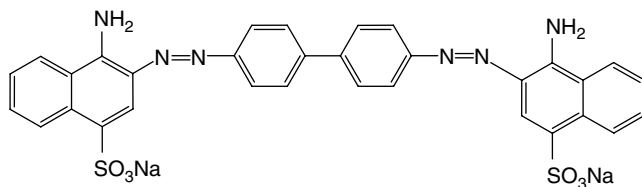
It was appreciated that continual revisions of the *Colour Index* would be necessary and was thought desirable by the Society to publish additions and corrections to the first edition before the preparation of a second edition. During 1943 and 1944 discussions within the Society were held to agree upon sponsoring a new *Colour Index*. The involvement of the American Association of Textile Chemists and Colorists (AATCC) began and collaboration between the Association and the Society resulted in the formation of a Colour Index Committee. The AATCC was responsible for all information from manufacturers on the whole of the American continent while the Society was responsible for all other manufacturing countries and for publication of the Index. The second edition of the *Colour Index* was published in 1956, just in time to coincide with the centenary of Perkin's discovery of Mauve. Only one volume was available in 1956 with Volumes 2 and 3 following in 1957 and Volume 4 in 1958. To keep the second edition of the *Colour Index* up to date, 'Additions and Amendments' were published in 1958 and continued publication of the 'A & A's in January, April, July and October; eventually a supplementary volume was issued which increased the number of generic names to 5481 and commercial names to 32 256 entries. Most important to the supplement was a new usage group entitled 'Reactive Dyes'. By 1963 the second edition of the *Colour Index* had been supplied to 51 countries and the supplement to 42 counties; eventually it went out of print during 1970. Due to the considerable sales of the second edition and the increasing changes in the information published within the now quarterly A & A's, information was gathered for a third edition during 1965. Again there was involvement from the AATCC, and advice was given by the Oil and Colour Chemists Association (OCCA) regarding

a 'Solvent Dye and Pigment Section'. The completely revised third edition of the *Colour Index* was published in November 1971 in five volumes containing 7900 generic names and 36 000 commercial names. The publication was in three parts: Part I, Volumes 1–3 (Technology; Classification by usage), Part II, Volume 4 (Chemistry; Classification by structure, and index of intermediates) and Part III, Volume 5 (Commercial indexes).<sup>3</sup> The main difference between the second and third editions is that in the third edition the technological information was separated from the commercial information. The latter is in Volume 5 and the related commercial names are arranged under each C.I. Generic Name as well as alphabetically. This was intended to simplify further revisions of the index, particularly revisions of Volume 5. Volume 6 was published in 1974 which supplemented the chemical and technological information of Volumes 1–4; this brought the total number of commercial names to 38 000. In 1982 a special volume of *Pigments and Solvent Dyes* was published. With the advancement and increased commercial use of computers, the third edition of the *Colour Index* was put onto CD ROM in 1997. The first DOS-based disks were scanned copies of the paper-based third edition but it was possible to search the index under both commercial and generic names. A fourth Microsoft Windows-based edition followed a few years later which was a much more user-friendly version and the interface had been radically updated to give smoother, faster searching. The World Wide Web became a valuable source of information and would enable an online version of the *Colour Index* to be continually updated by the Society and present users with a variety of subscription offers. The fourth edition of the *Colour Index* went online in 2000 and is still currently (2010) the version available through subscription to the Society of Dyers and Colourists.

## 1.7 Classification of dyes by dye class

### 1.7.1 Direct dyes

These dyes are still widely used for dyeing cotton because of their ease of application, wide shade gamut and relatively low cost. Following William Perkins's synthesis of *Mauvine*, there was still a need for mordanting cotton in order to dye it, except in a few cases where natural colourants such as Annato, Safflower and Indigo were used. The synthesis of an azo dye with substantivity to cotton by Griess was of great importance because mordanting was not necessary to apply this dye. In 1884 Boettiger prepared a red disazo dye from benzidine which dyed cotton 'directly' from a dyebath containing sodium chloride. The dye was named Congo Red by Agfa (C.I. Direct Red 28); its chemical structure is given in Fig. 1.2.<sup>4</sup>



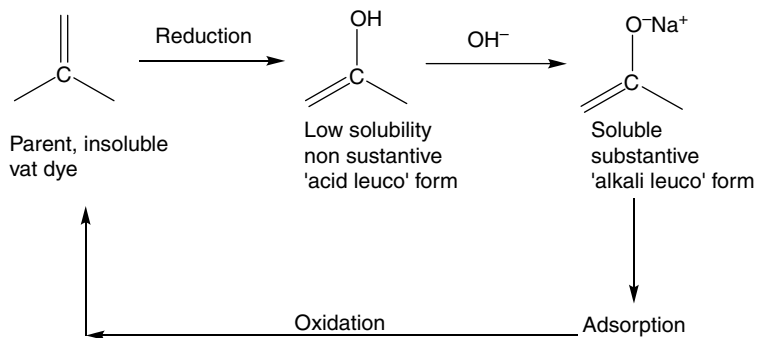
1.2 Congo Red C.I. Direct Red 28.

Direct dyes are classified according to many parameters such as chromophore, fastness properties or application characteristics. The major chromophoric types are as follows: azo, stilbene, phthalocyanine, dioxazine and other smaller chemical classes such as formazan, anthraquinone, quinoline and thiazole. Although these dyes are easy to apply and have a wide shade gamut, their wash-fastness performance is only moderate; this has led to their replacement somewhat by reactive dyes which have much higher wet and washing fastness properties on cellulosic substrates.

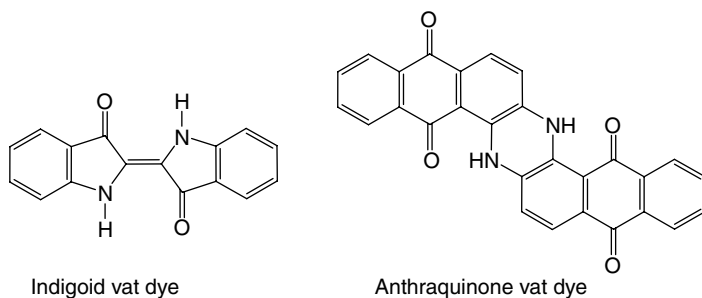
### 1.7.2 Vat dyes

These dyes are essentially water-insoluble and contain at least two carbonyl groups (C=O) that enable the dyes to be converted by means of reduction under alkaline conditions into a corresponding water-soluble 'leuco compound'. It is in this form that the dye is absorbed by the cellulose; following subsequent oxidation the leuco compound regenerates the parent form, the insoluble vat dye, within the fibre. This is represented simply in Fig. 1.3.

The most important natural vat dye is Indigo or Indigotin found as its glucoside, Indican, in various species of the indigo plant *indigofera*. Vat dyes are used where very high light- and wet-fastness properties are required. The typical chemical structures of vat dyes are given in Fig. 1.4.



1.3 Reactions of vat dyes.



1.4 Chemical structures of vat dyes.

Derivatives of indigo, mostly halogenated (especially bromo substituents) provide other vat dye classes including: indigoid and thioindigoid, anthraquinone (indanthrone, flavanthrone, pyranthone, acylaminoanthraquinone, anthrimide, dibenzathrone and carbazole).<sup>5</sup>

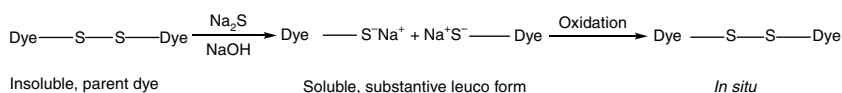
### 1.7.3 Sulphur dyes

Sulphur dyes are used for dyeing deep muted shades and offer good wet-fastness and moderate to good light-fastness. These dyes are very complex in structure and for the main part are unknown; the majority are prepared by thionation of various aromatic intermediates. The first commercial sulphur dye marketed as Cachou de Laval (C.I. Sulphur Brown 1)<sup>6</sup> was prepared by Croissant and Bretonnière in 1873 by heating organic refuse with sodium sulphide or polysulphide. However Vidal obtained the first dye in this class from intermediates of known structure in 1893.

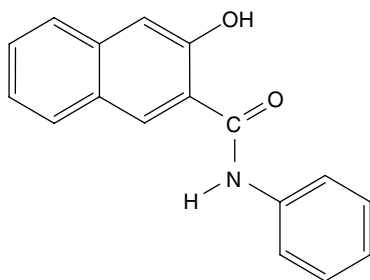
According to the *Colour Index* sulphur dyes can be divided into four groups: C.I. Sulphur dyes (water-insoluble), C.I. Leuco Sulphur dyes (water-soluble), C.I. Solubilised Sulphur dyes (highly water-soluble) and C.I. Condense Sulphur dyes (now obsolete). Figure 1.5 shows the dyeing reactions of the C.I. Sulphur dye.<sup>7</sup>

### 1.7.4 Azoic dyes

Azoic colourants are water-insoluble azo compounds produced *in situ* in the textile fibre by the interaction of a diazonium compound with a coupling



1.5 Dyeing reactions of a sulphur dye.



1.6 C.I. Azoic coupling component 2.

component. Azoic colourants are used for bright shades especially in the orange-scarlet-red region, with some navy and black shades. The actual hue produced with these colourants is determined by the particular combination of diazo and coupling components used.

The first azoic colourant was discovered in 1880 by Thomas and Robert Holiday of Read, Holiday & Co. (*Vacanceine Red*).<sup>8</sup> Cotton was impregnated with an alkaline solution of 2-naphthol and coupled with diazotised 2-naphthylamine. In 1912 a new coupling component was introduced, the anilide of 3,2-hydroxynaphthoic acid by Winter, Laska and Zitscher; this was commercially introduced by Griesham Elektron Co. under the name *Naphthol AS* (C.I. Coupling Component 2)<sup>9</sup> and is shown in Fig. 1.6.

Coupling components are primarily based on arylamides of 2,3-hydroxynaphthoic acid and were given the name of 'azoic' to describe their combinations with diazotised amine. A key feature of coupling components is their substantivity to cotton which enables them to be developed within the fibre without intermediate drying.

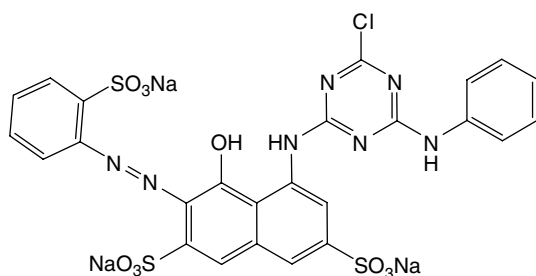
The diazo components are primary aromatic amines and marketed as 'Fast Colour Bases', for easily diazotised amines in the form of free base, hydrochloride or sulphate, and as stabilised diazonium compounds, 'Fast Colour Salts'. An example of the diazonium compound is C.I. Azoic Diazo Component 4 (Fast Red B Salt);<sup>10</sup> the colour code name of the diazonium compound is derived from the hue obtained when it is coupled with the coupling component, in this case C.I. Azoic Coupling Component 2.

## 1.7.5 Reactive dyes

### *Monochloro-s-triazine dyes*

These dyes are produced by the reaction of a dichloro-*s*-triazine dye with an amine at temperatures in the region of 25–40°C, resulting in the displacement of one of the chlorine atoms, producing a less reactive monochloro-*s*-triazine (MCT) dye.

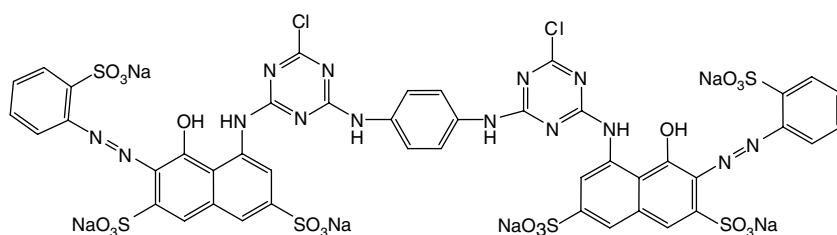
These dyes are applied in the same manner to cellulose except that, being less reactive than the dichloro-*s*-triazine dyes, they require a higher temperature (80°C) and pH (pH 11) for fixation of the dye to the cellulose to occur. A typical MCT structure is shown in Fig. 1.7.



1.7 MCT dye (C.I. Reactive Red 3).

### *Bis(monochloro-s-triazine) dyes*

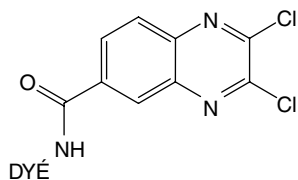
These types of dyes have two chromogens and two MCT reactive groups, therefore having much higher substantivity for the fibre compared to the simple MCT type dyes. This increased substantivity allows them to achieve excellent exhaustion onto the fibre at the preferred dyeing temperature of 80°C, leading to fixation values of 70–80%. Dyes of this type were and still are marketed under the *Procion HE* range of high-efficiency exhaust dyes. A typical bis MCT dye structure is shown in Fig. 1.8.



1.8 Bis(monochloro-*s*-triazine) dye (C.I. Reactive Red 120).

### *Dichloroquinoxaline dyes*

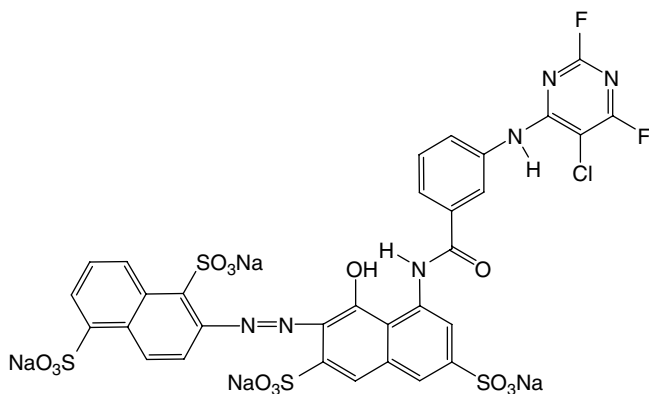
These dyes were introduced by Bayer, now Dystar, under the name *Levafix E*, and are based on the quinoxaline ring (Fig. 1.9). They are slightly less reactive when compared with the dichloro-*s*-triazine dyes and are applied at 50°C, but are susceptible to hydrolysis under acidic conditions.<sup>11</sup>



1.9 Typical dichloroquinoxaline dye.

### 2,4-Difluoro-5-chloro-pyrimidine dyes

Difluoromonochloro-pyrimidine dyes were introduced by Bayer (now Dystar) as the *Levafix EA* range and Sandoz (now Clariant) as the *Drimarene R* and *K* dye ranges. The greater electronegativity of the fluorine atom compared with that of chlorine results in a higher level of reactivity than that of chloro compounds. The dyeing temperature for application of these dyes is in the range of 40–50°C and they are classed as ‘cold dyeing’ dyes. The dye–cellulose fibre bond formed by these dyes is more stable to acid hydrolysis compared to that formed from the dichloro-*s*-triazine types, but does tend to undergo oxidative cleavage under the influence of light in the presence of perborates. A typical structure of this type of dye is given in Fig. 1.10.

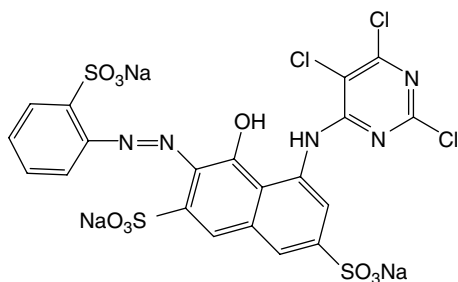


1.10 2,4-difluoro-5-chloro-pyrimidine dye (C.I. Reactive Red 147).

### 2,4,5-Trichloro-pyrimidine dyes

These dyes were launched by Sandoz (now Clariant) under the name of *Drimarene Z* and *X* and are based on the pyrimidine ring incorporating three chlorine atoms. These dyes have low reactivity and consequently require a dyeing temperature of 80°C for application. A typical structure of this type of dye is shown in Fig. 1.11.



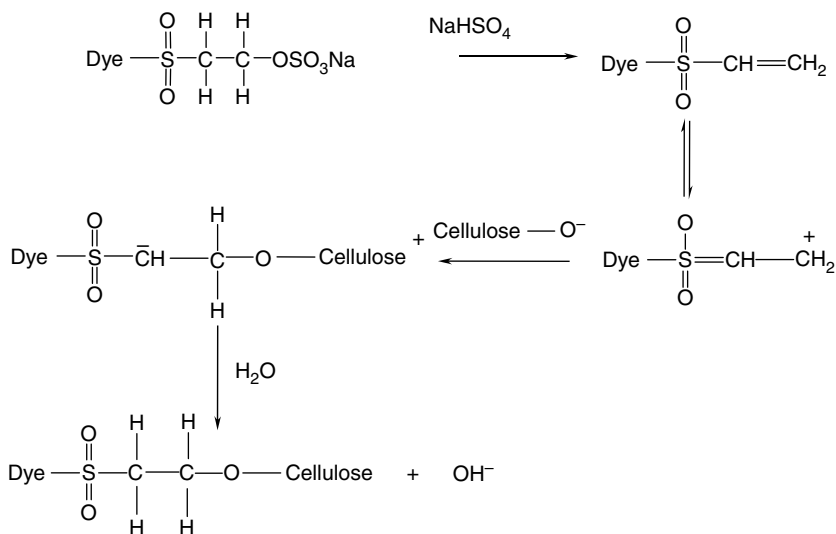


1.11 Trichloro pyrimidine dye (C.I. Reactive Red 17).

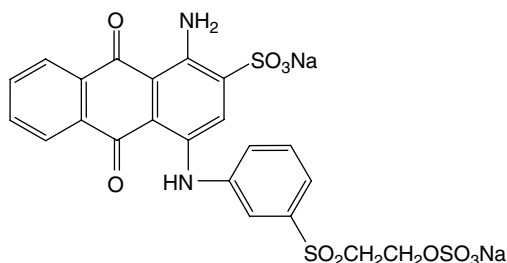
### Vinyl sulphone dyes

A major group of reactive dyes is based on the vinyl sulphone reactive system.<sup>12</sup> This group of dyes differs from the halogenoheterocyclic reactive dyes in that they function by means of a nucleophilic addition mechanism rather than the nucleophilic substitution mechanism utilised by the previous classes of dyes discussed.

These dyes were first introduced by Hoechst (now DyStar) and are still marketed under the name *Remazol* and contain a  $\beta$ -sulphatoethylsulphone grouping that, under alkaline conditions, eliminates bisulphate anion producing a vinyl sulphone group. Figure 1.12 shows the mechanism by which these dyes form the dye-fibre bond.

1.12  $\beta$ -elimination of  $\beta$ -sulphatoethylsulphone to vinyl sulphone and reaction with cellulose.

The level of reactivity of these dyes lies between that of the mono- and dichloro-*s*-triazine dyes, requiring an exhaust dyeing temperature of 60°C. The substantivity of these dyes for cellulose is lower than the halogeno-heterocyclic dyes since, unlike the heterocyclic ring, the vinyl sulphone grouping has little affinity for the fibre. This lower substantivity aids in the ease of removal of unfixed or hydrolysed dye at the end of the application process. Another advantage of this type of dye compared to the triazinyl types is their higher stability under acidic conditions; however the sulphonyl ethyl-cellulose dye-fibre bond may break down under alkaline conditions.<sup>11</sup> A typical vinyl sulphone dye structure is shown in Fig. 1.13.



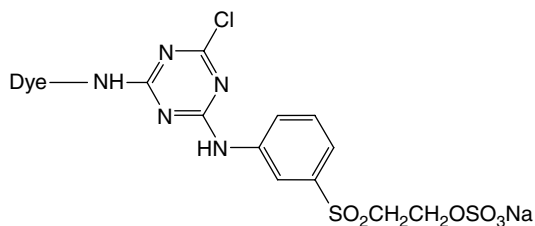
1.13 Vinyl sulphone dye (C.I. Reactive Blue 19).

### *Bifunctional reactive dyes*

Bifunctional reactive dyes are dyes which contain two reactive groups, thus enhancing the possibilities of reaction with the fibre, leading to greater fixation and less hydrolysed dye. Although the term *bifunctional* has become widespread over the last twenty years, the first bifunctional dye was launched back in 1957 when Hoechst (now DyStar) produced *Remazol Black B* (C.I. Reactive Black 5)<sup>12,13,14</sup> which contained two sulphatoethylsulphone groupings. Other ranges containing two groupings of the same character were launched by other manufacturers, most notably I.C.I. with the *Procion HE* bis(monochloro)-*s*-triazine type, described earlier. Bifunctional reactive dyes can be subdivided into two categories; *homobifunctional* (dyes that contain two identical reactive groups) and *heterobifunctional* (dyes containing two reactive groups of different types). Homobifunctional dyes have been covered earlier in for bis(monochloro-*s*-triazine) dyes, and the bis ( $\beta$ -sulphatoethylsulphone) dye *Remazol Black B*.

The first heterobifunctional reactive dye range was launched in 1979 by Sumitomo under the trade name *Sumifix Supra*.<sup>15</sup> This dye range contained dyes with a  $\beta$ -sulphatoethylsulphone grouping and an MCT group; a general structure is shown in Fig. 1.14.

Fixation of the dye to the fibre can take place by reaction of the cellulosate anion with either reactive group, although because of the higher



1.14 General structure of Sumifix Supra dyes.

reactivity of the vinyl sulphone group, it makes a greater contribution to dye–fibre fixation. The MCT group contributes to substantivity, while the  $\beta$ -sulphatoethylsulphone grouping gives dye–fibre bonds of enhanced stability towards acid hydrolysis. The application temperatures for these dyes is in the region of 50–80°C due to the difference in reactivity between the two reactive groups, lower temperatures favouring reaction via the vinyl sulphone and higher temperatures via the MCT group.

In 1988 Ciba launched their version of the heterobifunctional reactive dye in the *Cibacron C* dye range. These dyes contain an aliphatic vinyl sulphone group together with either a monofluoro-*s*-triazine group or an aromatic vinyl sulphone group. The range is well suited for pad application due to their low to medium substantivity combined with high fixation and easy wash-off properties.<sup>16</sup>

## 1.7.6 Acid dyes

### *Non-metallised dyes*

These dyes can be applied to nylon, wool or silk in the pH range 3.0–7.0. The wet-fastness of these dyes varies from moderate to good and their light-fastness is generally in the blue-scale range 5.0–6.0.<sup>17</sup>

These small relative molecular mass (*Mr*) dyes are applied at low pH values so that dye–fibre substantivity arises from ion-ion electrostatic forces, for example, in nylon operating between the amino end group, which is protonated under acidic conditions and the anionic dye. Under these conditions the dyes display very good migration and levelling characteristics, but low wet-fastness. Dyes which have larger *Mr* exhibit higher substantivity for the fibre, but the migrational properties are lower although a higher wet-fastness is achieved with these dyes.

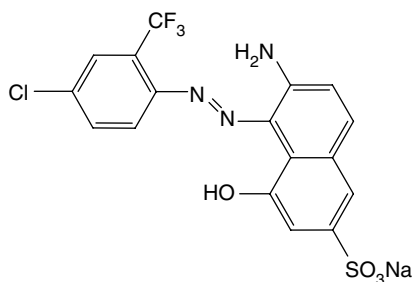
These dyes have been divided into three subgroups due to their varying application and fastness properties. Stevens<sup>18</sup> used a I–III grouping for classifying non-metallised acid dyes on nylon:

Group I: Dyes with little affinity under neutral or weakly acidic conditions, but which exhaust under strong acid conditions.

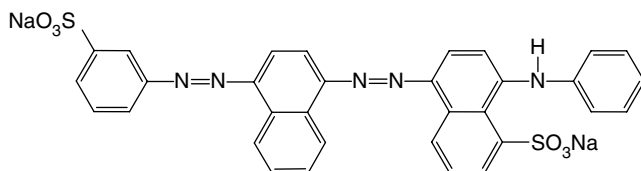
Group II: The largest group of dyes that exhaust onto nylon within the pH range 3.0–5.0.

Group III: Dyes that exhibit a high affinity for nylon under neutral or weakly acid conditions (pH 5.0–7.0).

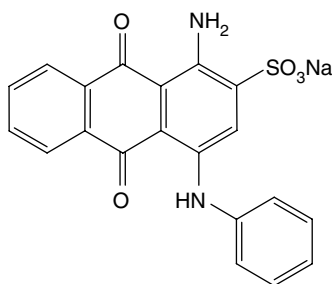
The water solubility of these dyes is due to the presence of one or more sulphonate groups ( $-\text{SO}_3\text{Na}$ ). These dyes belong to the azo chemical class which represents the largest class of dyes, providing an extremely large gamut of shades. Three examples of these dyes are shown in Figs. 1.15–1.17.



1.15 C.I. Acid Red 266 (monoazo).



1.16 C.I. Acid Blue 113 (disazo).



1.17 C.I. Acid Blue 25 (anthraquinone).

There are several disadvantages associated with non-metallised dyes for some substrates: for example on nylon, low colour yield, lower wet-fastness properties and the tendency to barré dyeing. Also, due to the lower crystallinity of nylon 6 compared to that of nylon 6,6, dyes show a greater rate of uptake on nylon 6 for a given pH range.

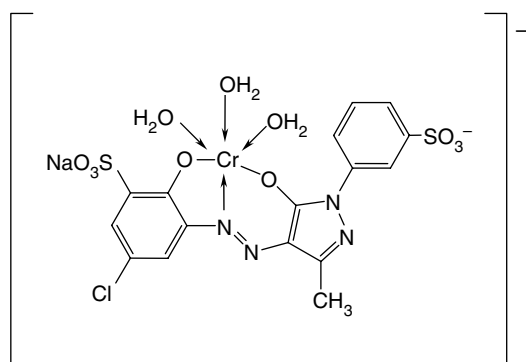
Non-metallised dyes vary in their ability to cover barré nylon. In general low Mr dyes exhibit better coverage than their higher Mr counterparts. Thus by careful dye selection it is possible to greatly minimise or even eliminate the effects of physical variations within the fibre. Eliminating chemical variations is more difficult to achieve.

The limited number of amine end groups (AEG) in the nylon fibre dictates the saturation value of the fibre by the non-metallised acid dyes. Once a dye anion has been attached to an amino group on the fibre, that group is 'neutralised' by the dye anion and so is unable to attract further dye anions.

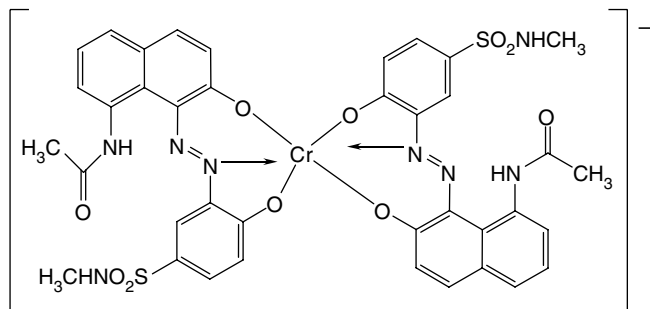
### *Metal-complex dyes*

These dyes are based upon mordant dyes; the difference is that metal-complex dyes have the mordant metal incorporated within the dye molecule so do not require a separate mordanting stage. There are two classes of metal-complex dyes – 1:1 metal-complex and 1:2 metal-complex dyes. As the names suggest, the metal-complex dye comprises one metal atom (usually chromium) coordinated with one or two molecules of a dye ligand. An example of each metal-complex structure is shown in Figs. 1.18 and 1.19.

The 1:1 metal-complex dyes are applied under strongly acidic conditions for satisfactory migration to take place. These conditions can cause severe degradation of nylon fibres and this limits the use of these dyes for dyeing nylon. A few dye manufacturers have tried to overcome this problem



1.18 C.I. Acid Red 183 (1:1 metal-complex).



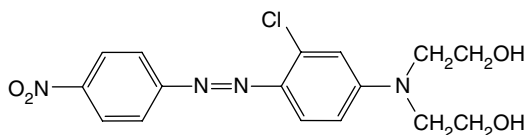
1.19 C.I. Acid Black 60 (1:2 metal-complex).

by either using sulphamic acid in place of sulphuric acid or by the inclusion of a levelling agent to reduce fibre damage; these are described by Burkinshaw.<sup>19</sup>

The 1:2 metal-complex dyes exhibit high saturation values and excellent compatibility in mixture shades and they have good light-fastness and wet-fastness properties. However, their ability to cover chemical variations within the fibre varies significantly and is dependent upon molecular size and substituent solubilising groups. The shade gamut of these dyes is restricted to dull shades and the class is deficient in bright blues and reds. There is a wide range of 1:2 metal-complex dyes available for nylon; different manufacturers' ranges differ in optimum pH range but they are generally applied from a neutral to weakly acidic dyebath.

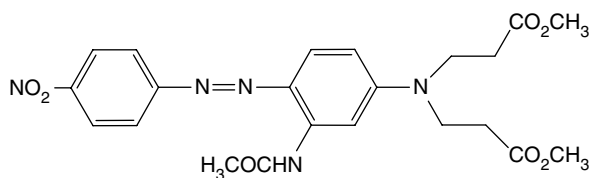
### 1.7.7 Disperse dyes

These dyes are frequently insoluble or sparingly soluble in water, non-ionic in character and applied to hydrophobic fibres from an aqueous dispersion.<sup>20</sup> They are predominantly used on polyester but have found application to nylon, cellulose acetate and acrylic fibres, although some of the wet-fastness properties of the dyes on these substrates are poor. The dyed substrate is usually given a reduction clear following dyeing, in order to clean the substrate surface of dye that would cause staining if left untreated. These dyes were traditionally applied to polyester at the boil with the inclusion of a carrier in the dyebath to facilitate diffusion of the dye into the substrate. Carriers caused many problems to the dyer including residual smell of carrier on fabrics and reduced light-fastness of dyed fabrics due to residual carrier. Since the advent of pressurised dyeing machines, these dyes are now applied to polyester without carriers at temperatures around 130°C; the reduction clear is still conducted after dyeing. A typical disperse dye structure is shown in Fig. 1.20.



1.20 Chemical structure of a disperse dye (C.I. Disperse Red 7).

The reduction clear is an extra cleaning step which increases processing time and cost together with adding to the effluent load from the dyeing process. There have been attempts to create dyes that become water-soluble in mildly alkaline conditions in order to eliminate the reduction clear process. The Dispersol C dyes from DyStar are one such brand. These dyes had either a sulphonyl fluoride or, more commonly, a number of carboxylate ester groups on the molecular structure of the dye. During alkaline scouring after dyeing these groups are converted to their water-soluble sulphonic/carboxylic acid forms rendering the dyes water-soluble, therefore dye which was still on the surface of the substrate would be dissolved in the wash-off liquor and the result would be a clean surface of the substrate. An example of the Dispersol C dyes is shown in Fig. 1.21.



1.21 Chemical structure of an alkali-clearable disperse dye (C.I. Disperse Red 278).

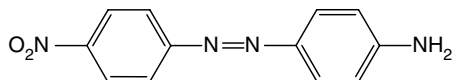
Disperse dyes have also been used in thermal transfer printing. This can be conducted using several methods.

### *Pad themofix*

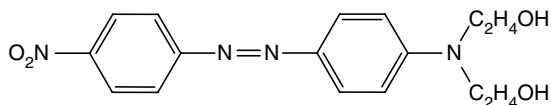
The fabric is padded with dye dispersion and following drying, subjected to a high temperature for a short duration (typically 30–60 s) whereby the dye diffuses into the substrate. The selection of dyes able to undergo sublimation is critical for this process; this rules out the use of the ‘high energy’ type of disperse dyes.

### *Paper transfer printing*

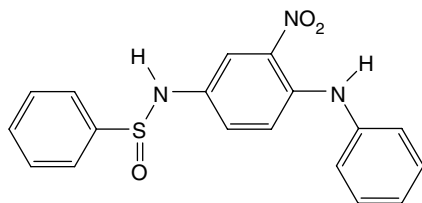
The design required is printed in reverse on a transfer paper. The paper is placed firmly against the substrate which passes between two pressurised heated rollers. The design on the paper is transferred to the substrate via sublimation of the dyes.



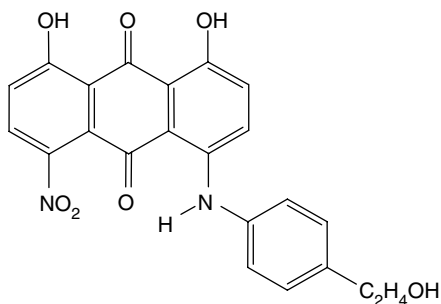
1.22 Class A disperse dye (C.I. Disperse Orange 3).



1.23 Class B disperse dye (C.I. Disperse Red 19).



1.24 Class C disperse dye (C.I. Disperse Yellow 42).



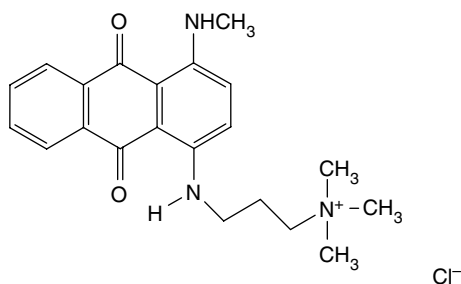
1.25 Class D disperse dye (C.I. Disperse Blue 27).

Disperse dyes are classified by their sublimation temperature: Class A dyes have the lowest sublimation temperature whilst Class D dyes have the highest sublimation temperature. The sublimation temperature is also relative to the molecular size of the dyes. Class A dyes are relatively small in molecular size whilst Class D dyes are significantly larger than Class A dyes. Examples of disperse dyes from Class A to Class D dye are shown in Figs. 1.22–1.25.

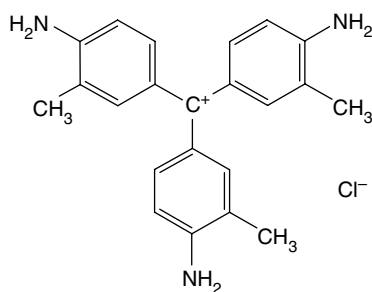
### 1.7.8 Basic dyes

These dyes are usually applied to acrylic, paper and nylon substrates, but can also find use in some modified polyester substrates.<sup>21</sup> Basic dyes are





1.26 Localised charge basic dye (C.I. Basic Blue 22).



1.27 Delocalised charge basic dye (C.I. Basic Violet 2).

water-soluble and produce coloured cations in solution; these cations are attracted electrostatically to substrates with a negative charge. Basic or cationic dyes can have either the positive charge localised on an ammonium group (these dyes are characterised by a high tinctorial strength), or it can be distributed as a delocalised charge over the dye cation as found in many triarylmethane, xanthenes and acridine dyes. Examples of a localised and a delocalised charge dye are given in Figs. 1.26 and 1.27, respectively.

Basic dyes are often applied with retarders due to their poor migration properties at the boil. This poor migration is due to the high substantivity of the dye for the substrate and rapid increase in diffusion at high temperatures. Careful control is necessary when using retarders so that anionic sites within the substrate are not blocked which would restrict dye uptake making it difficult to achieve dark shades.

## 1.8 Conclusion

As stated in the introduction, this chapter only gives generic chemistry and applications of the different classes of dyes used in the textile colouration industry. In Volume 1, 'Principles, processes and types of dyes', the chapters in Part I follow the preparation of substrates for dyeing, the chemistry of

dyeing and the thermodynamics of dyeing systems. In Part II each dye class is described in detail giving more specific information regarding the chemistry of the dye class and the most common mode of application. In Volume 2, 'Application of dyes', the chapters cover the application of dyes to the textile industry and also other colour-related industries such as plastics, cosmetics, ink-jet printing, medical applications, foodstuffs, electronic applications and photographic dyes. Textile and industrial dyeing is a vast subject and there are many books which specialise on one specific topic. It would be unwise to try and produce a volume that encompasses every aspect of the dyeing industry; new technologies are constantly being cited in related journals and the quantity of research and development globally means that the subject of textile and industrial dyeing is in constant flux. There are many references at the end of each chapter which will guide the reader to additional sources of information in order to gain a broader knowledge of the subject.

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**Abstract:** This chapter provides an overview of structural and physical properties of some natural and man-made fibres which are important in conjunction with their processing into yarns, dyeability and general end-use. Fibre properties such as linear density, length and strength are considered in terms of their effects on yarn properties. Yarn spinning systems are briefly characterised; general yarn properties are discussed in relation to the various end-uses. Phases and possible scenarios of dyeing process for different types of fibres are outlined. Physical structure and intermolecular bonds of polymers are introduced. Chemical composition, physical structure and technical characteristics of the main types of fibres are discussed.

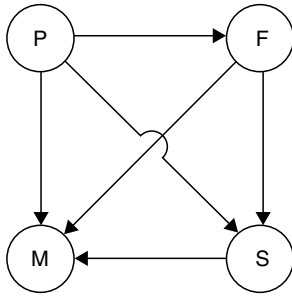
**Key words:** fibre, cotton, wool, silk, viscose, polyester, nylon, acrylic, dyeability, yarn, spinning system, polymer structure, intermolecular bonds, wettability.

## 2.1 Introduction

Textiles constitute a large and diverse group of materials which have been widely used in apparel, domestic, medical and technical applications. The application of colour to textiles, in particular in fashion, is a multidimensional area of activity where aesthetical, social, psychological, creative, scientific, technical and economic aspects come together in the design of the final product. Textile coloration is truly the area where Science and Technology meet Creativity.

Textiles are specific types of materials characterised by a unique combination of properties including strength, flexibility, elasticity, softness, durability, heat insulation, low weight, water absorbency/repellence, dyeability and resistance to chemicals. Textiles are inhomogeneous and unisotropic materials displaying highly non-linear viscoelastic behaviour and dependence on temperature, humidity and time. In addition to this all textile materials without exception have a statistical nature so that all their properties are characterised by (sometimes unknown) distribution.

In broad terms, properties of textile materials depend on physical and chemical properties of the fibres from which they are made and on material



2.1 Relationships between production process (P), properties of fibre (F), material structure (S) and resultant material properties (M).

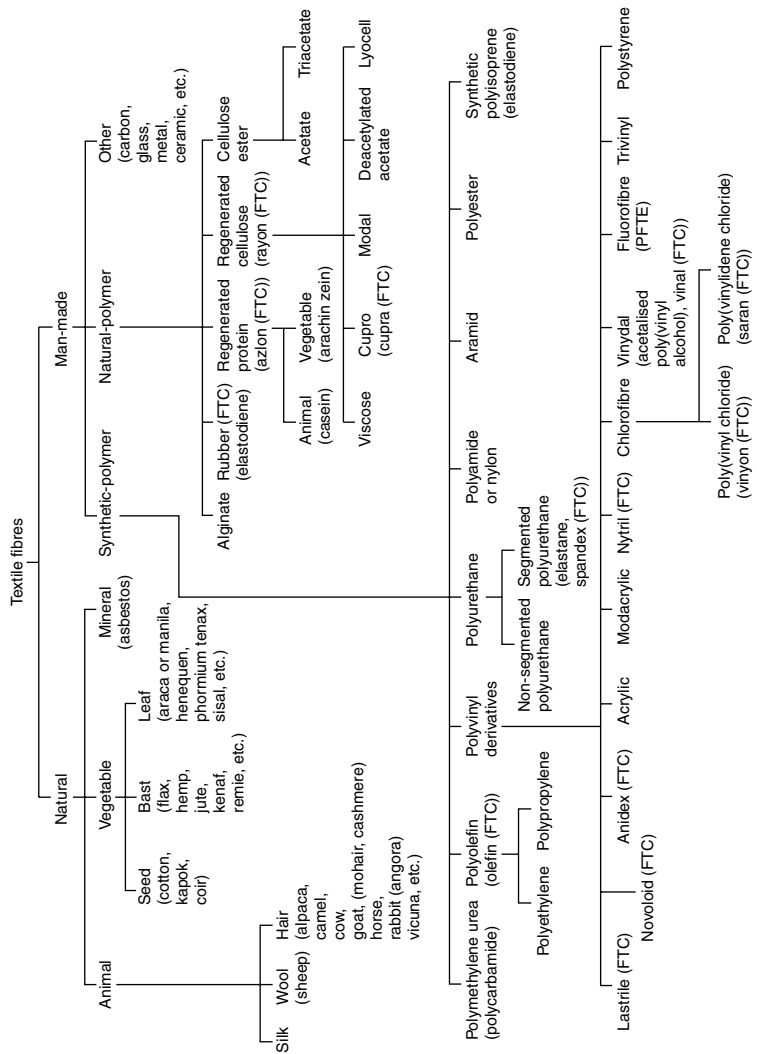
structure where the latter is defined both by the fibre properties and the production process which in turn may affect the fibre properties on their way through the processing line. Figure 2.1 shows links between parameters of production process (P), properties of fibre (F), material structure (S) and resultant material properties (M).

This chapter will consider properties of textile fibres which are important in terms of their conversion into the yarns and in terms of their dyeability.

## 2.2 Classification and properties of textile fibres

Despite the diversity of the physical and structural forms in which they come and chemical composition of the substances from which they are made the technology of producing all textile materials starts from the same initial point which is fibres. Textile Terms and Definitions (Denton and Daniels, 2002) define textile fibre as a textile raw material generally characterised by flexibility, fineness and high ratio of length to thickness. It is estimated that some 90% of all fibres are first spun into yarns, which are then converted into fabrics, and only about 7% of fibres are directly used for the manufacture of the end-use products (Lawrence, 2003). Processes used for the production of textile materials can be subdivided into four main groups as follows:

1. Production of fibres which can be natural or man-made.
2. Production of yarn where certain technical differences exist in spinning cotton, wool, synthetic fibres and fibre blends.
3. Manufacture of woven, knitted and nonwoven fabrics, carpets, webs and other sheet materials.
4. Fabric finishing which includes bleaching, dyeing, printing and special treatments aimed at giving the final product specific properties like water repellency and anti-bacterial and fire-retardant properties.



## 2.2 Fibre classification.

Traditionally fibres are classified according to their origins. Thus fibres can be (i) natural, which in turn are subdivided into vegetable, animal and mineral and (ii) man-made, which are produced from natural or synthetic polymers, and others such as carbon, ceramic and metal fibres. A detailed classification of fibres is presented in Fig. 2.2 (Denton and Daniels, 2002). This classification is continuously updated mainly due to the advances in the manufacture of man-made fibres.

The manufacture of fibres, be they natural or man-made, is a large and interesting topic by itself but it will not be considered in this chapter. The starting point will be fibres as a raw material supplied to the textile industry.

The application of colourants, be they dyes or pigments, to textiles can be done at different stages on the route of converting fibres into the final product. Fibres can be dyed in the form of loose mass and then used in the manufacture of either solid shade or melange yarns. In this case particular care must be taken not to cause any damage to the fibres because this may create difficulties in spinning.

There are several possible scenarios for fibre dyeing as follows:

1. Dyeing a loose mass of single fibre, for example, 100% cotton or 100% wool. This may seem to be the simplest case but nevertheless the variation in fibre properties may cause variation in the resultant colour between the batches.
2. Dyeing fibre mixtures of similar origins by the same type of dyes, for example, cellulose fibre mixtures or protein fibre mixtures. The difficulty here is to achieve the same colour depth in all components. For this dyes must be specifically selected in order to equalise the differences in fibre dyeability.
3. Dyeing fibre mixtures of different origins where it is possible to obtain colour effects by dyeing each component to a different colour. In this case it is necessary to provide uniform fibre mixture before the dyeing; an additional re-mixing after dyeing may still be required.
4. Dyeing the natural and synthetic fibre blends where typical cases are cotton/polyester, wool/polyester, wool/acrylic and wool/polyamide blends. The selection of fibres for these blends can be explained by the complementary properties of the components. These blends represent a considerable proportion of textiles used for apparel due to lower production cost, good comfort characteristics, improved durability and better dimensional stability in comparison to 100% natural and 100% synthetic fibre products.

In many cases blend components can be dyed separately in the form of worsted top as in wool processing and then mixed in spinning.

Dyes may be applied to the yarns in the form of hanks or closely wound packages where again care should be taken over preserving yarn structure and

mechanical characteristics which then will be important in weaving and knitting. In this way it is possible to produce solid shade yarns which can be twisted in order to achieve desirable colour effects. Alternatively, fancy colour effects can be produced using the space dyeing technique (Gong and Wright, 2002).

Woven and knitted fabrics can be dyed to achieve a solid shade throughout the fabric structure or a variety of patterns can be printed on the fabric surface. The fibre composition of yarns and fabrics affects the dyeing processing methods in a similar way as was mentioned above with regard to dyeing loose fibre mass.

Fibres must have a combination of properties which make them suitable for spinning, dyeing and further conversion into the fabric so that a diversity of performance characteristics can be achieved in commercially viable end-use products.

Let us first consider fibre properties which are important for their successful conversion into the yarn since this is the main starting material for the production of fabrics.

### **2.3 Fibre properties related to textile technology**

Major fibre properties which define the processing route for fibres in spinning and the quality of the resultant yarn are as follows.

1. **Fibre length.** All natural fibres have a limited length and are often referred to as staple fibres. Typical values of fibre length are 30 mm for cotton and 80 mm for wool. Man-made fibres initially are produced as continuous filaments theoretically of unlimited length but may be cut into small lengths thus becoming staple man-made fibres. Fibre length affects yarn strength because longer fibres provide greater number of contact points between individual fibres where friction forces develop and hold fibres together. For this reason fibres shorter than 12 mm are generally considered not to be suitable for spinning although special spinning methods implemented by the DREF system, which is the abbreviation of Dr E Fehrer who invented this system (Lunnenschloss and Brockmanns, 1985) can successfully produce thick yarns from short fibres. All yarns produced from staple fibres have a degree of hairiness which increases with the increase of fibre length. Excessive hairiness makes the yarn difficult to use in knitting, weaving and sewing because short lengths of fibres may be cut off and get accumulated in thread guides causing yarn breakage.
2. **Fibre diameter.** This is measured in microns usually denoted as  $\mu\text{m}$  which is 1/1000 of a millimetre. Typically natural fibres are from 6  $\mu\text{m}$  (silk) to 15  $\mu\text{m}$  (cotton) to 70  $\mu\text{m}$  (thick wool) in diameter. Man-made fibres can be manufactured to any specified diameter and cross-sectional shape. Fibre diameter defines the minimum thickness of the staple fibre yarn



that can be achieved in spinning. At the same time using finer fibre for the manufacture of yarn of the same thickness is advantageous due to the increased number of fibres which contribute to the yarn strength. Fibre diameter has a significant effect on comfort in apparel production because using thicker fibres may cause a prickly sensation in contact with skin (Bishop *et al.*, 1997); this sometimes happens if low quality thick wool fibres are used. Finer fibres, on the other hand, are prone to the formation of entangled balls of fibres on the fabric surface called pilling.

3. Fibre tensile strength, tensile elongation and elastic recovery are basic mechanical properties which define strength, durability, ability to stretch and conform to complex shapes and ability to return to original shape and dimensions in all products made from the fibres. These properties are important for successful fibre processing where they are subjected to various external forces. Tensile strength is usually expressed in grams or centinewtons (cN), where  $1 \text{ cN} = 1.02 \text{ g}$ , tensile elongation is expressed as percentage of initial length, and tensile recovery as percentage reduction of extension observed after the applied force is removed. For example, individual cotton fibres have an average tensile strength of 4 cN.
4. Crimp is the waviness of fibre along its length. Crimp is a natural property of many natural fibres such as cotton and wool. Crimp helps in developing fibre cohesion in sliver, roving and yarn; an excessive crimp may cause difficulties in disentangling the raw fibre mass. Man-made fibres are initially produced as straight filaments but after that crimp can be developed by a specific treatment in order to improve fibre handle.
5. Friction coefficient is important for ensuring good fibre cohesion; this prevents fibre slippage with respect to each other thus making the yarn stronger. On the other hand, high friction coefficient makes the yarn difficult to process due to the friction forces that may develop between the moving yarn and yarn guides.
6. Accumulation of electrostatic charge is a negative property for any fibre because it results in a repulsive force between fibres and thus reduces fibre cohesion. Electrostatic charge also makes fibres difficult to process by causing fibres to stick to the working parts of spinning machinery.
7. Moisture regain characterises the amount of moisture which is retained by fibre depending on its chemistry, relative humidity and temperature of the atmosphere. Moisture regain helps in dissipating electrostatic charges which are often a problem with man-made fibres.
8. Impurities content in the raw fibre mass to a large extent affects stability of all spinning processes. Typical dimensions of impurities present in natural fibres such as cotton and wool are comparable to and often exceed the diameter of average yarn. In the case where such impurities remain in the fibre flow at the last stages of spinning they can cause excessive yarn breakage and may significantly reduce the quality of the final product.

It is necessary to take into account the fact that all fibres used in the textile industry, be they natural or man-made, are characterised by the variation of all their properties. This may cause a significant variation in the qualities of end-use products. It therefore makes sense to talk only about average characteristics of fibre properties which are the subject of continuous testing in industrial practice. Fibre testing, together with the testing of intermediate and final products, is an important part of quality control procedures.

In practical terms it is difficult to separate fibre properties which are important for spinning from those that affect the performance characteristics of the final product. For example, Table 2.1 compares properties of cotton, viscose and polyester. The analysis of this table shows that these three fibres are complementary in their properties; this explains why cotton/polyester blends are often used in the textile industry.

## 2.4 Classification and properties of basic textile products

Assembling individual fibres into the yarn which is followed by the conversion of the yarn into woven and knitted fabric brings about additional factors mainly related to the structural characteristics of these products which are important for dyeing. The following sections briefly discuss the main technical and structural parameters of yarns and fabrics.

Table 2.1 Comparative performance of cotton, viscose and polyester

Properties	Comparative rating		
	Cotton	Viscose	Polyester
<b>Comfort</b>			
Moisture regain	Good	Very good	Poor
Thermal protection	Good	Very good	Poor
Air permeability	Very good	Good	Poor
Softness	Good	Very good	Poor
Smoothness	Poor	Good	Very good
Dissipation of static electricity	Good	Very good	Poor
<b>Aesthetic</b>			
Drape	Good	Very good	Poor
Lustre	Poor	Very good	Very good
Crease recovery	Poor	Poor	Very good
Uniformity	Poor	Very good	Good
<b>Performance in wear</b>			
Resistance to pilling	Good	Very good	Poor
Wash and wear	Good	Poor	Very good

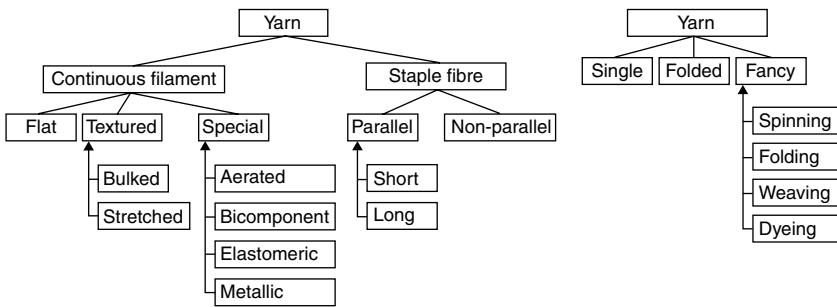
Source: <http://www.swicofil.com/products/200viscose.html>

### 2.4.1 Yarn classification and properties

A yarn may be defined as a product of substantial length and relatively small cross-section, made of fibres and/or filaments with or without twist which can be used for interlacing in processes such as weaving, knitting or sewing.

Yarns are classified according to the characteristics of the fibres from which they are spun, and the arrangement of individual strands in the finished yarn (see Fig. 2.3).

Continuous filament yarns are spun from a fibre-forming substance in a form of solution (viscose, acrylic) or melted polymer (polyester, polyamide). The polymer is extruded through the holes of a spinneret (Fig. 2.4) beyond which it solidifies in the small diameter filaments. Alternatively there is only one hole in a form of narrow slit so that the thin film is produced which is then divided into narrow strips. This process is essentially continuous.



2.3 Yarn classification.



2.4 An example of a spinneret.

Staple fibre yarns are made from short fibres bound together by twisting. These fibres can be natural (cotton, wool, jute, flax, silk) or man-made (viscose, nylon, polyester, acrylic). Staple fibre yarns are found in two forms:

1. Parallel fibre yarns where the fibres before twisting were straight and parallel to the axis of the product. This group can be subdivided into:
  - (a) Long staple fibre yarns which are spun from fibres from 25 mm to over 300 mm long but usually less than 150 mm. Typically these are combed yarns manufactured from wool and its blends.
  - (b) Short staple fibre yarns spun from fibres from 12 to 80 mm long. Fibres are usually thinner than those used for long staple yarn. Typically these are 100% cotton or wool carded yarns and their blends with synthetic.
2. Non-parallel (condenser spun) fibre yarns where fibres before spinning were not parallel but arranged in a random manner. This is the result of twist applied during the formation of roving alternately in opposite directions. It is difficult and sometimes almost impossible to untwist such a yarn up to the condition when fibres are completely disentangled. The condenser system is mainly used for spinning the blends of inhomogeneous fibres such as wool and acrylic.

#### 2.4.2 Basic operations in yarn spinning

Spun yarns are produced by placing a series of individual fibres or filaments together to form a continuous assembly of overlapping fibres, usually bound together by twist. 'Yarn Spinning System' is the collective term which describes the sequence of processes that are required to produce a yarn where spinning is the last process in the production of a single yarn. All natural fibres follow a similar basic routine of conversion to spun yarn which includes four major stages although man-made fibres do not require the cleaning which is necessary for natural fibres.

1. Pre-processing
  - (a) Sorting. This operation is required in wool spinning because different parts of the fleece contain fibres of different length and thickness. This is a largely manual operation performed by highly skilled personnel.
  - (b) Cleaning. This is necessary with all natural fibres in order to remove the impurities present in the raw fibre before further processing can take place. The cleaning process may be chemical (wool scouring in water-based emulsion), mechanical (removal of dry impurities from cotton), or a combination of the two, depending on the nature of the impurities.
  - (c) Opening and disentangling. Both natural and man-made fibres are delivered to the spinning mill in bales weighing on average some 200 kg which contain very closely packed fibres. Opening is necessary

for removing the impurities which are attached to the natural fibres. Opening is accompanied by disentangling.

- (d) Blending. This is necessary to ensure uniformity of the product by eliminating variations between different sources of fibres or in the case of man-made fibres between different production runs.

Pre-processing results in the formation of a product consisting of disjoint fibre tufts each only about 1 g in weight.

2. Formation of a continuous strand

This is usually performed by a carding process which separates fibre tufts into individual fibres and places them parallel to each other resulting in a carded web; this web then is transformed into a sliver (in cotton spinning) or top (in wool spinning). Sliver is a rope-like product containing thousands of fibres in any cross-section. The sliver does not have twist; fibres are held together by friction which provides sufficient strength due to the large number of fibres.

3. Reduction of strand thickness. There are two methods employed:

(a) Reduction by division. This method is used in the production of condenser spun yarns. The carded web of fibres is divided into narrow strips to which an alternating twist is applied resulting in a product called slubbing from which the condenser yarn is spun.

(b) Reduction by drawing. This involves the use of a drawing frame which performs drafting by a series of rollers rotating at progressively increased speeds. Drafting is combined with doubling (assembling a number of slivers parallel to each other) where doubling increases the thickness and improves uniformity whereas drafting reduces the sliver thickness but increases its irregularity. The best balance between these two tendencies can be achieved by doubling 8–10 slivers and applying approximately the same amount of drafting. The final product at this stage is a twisted roving.

4. Twist insertion. Sliver (in open-end spinning) or roving (in ring spinning) is converted into a yarn by reducing the thickness down to the required count and inserting twist to give necessary strength.

In technical terms, yarns are specified by their linear density (count), twist level and direction, and fibre composition. In addition to this the yarn properties which are important for further processing include strength, elongation at break and variation in linear density.

### 2.4.3 Yarn linear density, twist and strength

Yarn thickness is difficult to measure because of the ill-defined yarn surface, yarn hairiness and inherent compressibility. The thickness of the yarn

is important for setting up the weaving looms and the knitting machines for the production of fabric of specified weight and thickness. In commerce and industry the yarn thickness is identified by the quantity known as yarn count which links the mass and the length of yarn.

There are two main count systems:

1. Mass per unit of length. This is a direct method where a higher count means a thicker yarn. Tex system defines yarn thickness in terms of the weight in milligrams of 1 m long piece or the weight in grams of 1 km long piece. For example, 20 tex yarn refers to a yarn 1 m long piece which weighs 20 mg or 1 km long piece which weighs 20 g. Tex system is universal and can be used to express the thickness of any linear products. For example, the count of a typical cotton roving may be 1 ktex = 1000 tex, whereas a typical wool top may be of 10 ktex = 10 000 tex count. Thickness of individual fibres can also be expressed using Tex system. For example, cotton fibre may be of 0.15 tex count.
2. Length per unit of mass. This is an indirect method where a higher count number denotes a thinner yarn. There are several systems which are used in industrial practice, for example:
  - (a) Metric count defines yarn thickness in terms of the number of 1 km long pieces each weighing 1 kg.
  - (b) Bradford Worsted system defines yarn thickness as the number of 560-yard (1 yard = 0.9144 m) hanks each weighing 1 lb (453.6 g).
  - (c) English cotton system – the number of 840-yard hanks which weigh 1 lb each.

Yarn count expressed in the Tex system,  $T_t$ , can be converted into indirect system using conversion factors presented in Table 2.2 and simple equations as follows:

$$\text{Tex system count} = \frac{\text{Conversion factor}}{\text{Indirect system count}} \quad [2.1]$$

Table 2.2 Conversion factors

Yarn count system	Symbol	Conversion factor
Bradford Worsted	$N_{w}$	885.8
English Woollen (Yorkshire)	$N_y$	1938
English Cotton	$N_c$	590.5
Continental Metric	$N_m$	1000
Linen	$N_l$	1654

$$\text{Indirect system count} = \frac{\text{Conversion factor}}{\text{Tex system count}} \quad [2.2]$$

The conversion between Denier system (Td) and Tex system can be done using the following equation:

$$T_t = 0.1111 \text{ Td} \quad [2.3]$$

Yarn count defines the end-use of the yarn as shown in Fig. 2.5 (Lawrence, 2003).

It follows from the definition of the staple fibre yarn that the integrity of the yarn is provided by twist which is characterised by direction and twist level. Yarn twist direction (see Fig. 2.6) is identified by letters Z (for clockwise) or S (for anti-clockwise) twist. Yarn twist direction affects the appearance of the surface of woven and knitted fabric.

Yarn twist level is measured by the number of turns of twists per unit length which is 1 m in metric and SI units and 1 in. in Imperial units.

Yarn twist level has a significant effect on the density of fibre disposition in the yarn cross-section, on the yarn diameter and yarn strength.

All yarns, regardless of the technical specification, have a large degree of porosity where only some 80% of the yarn volume is occupied by fibres even in the case of ultimately densely packed fibres. Figure 2.7 shows the effect of twist and linear density on fibre distribution in the yarn cross-section (Grishanov *et al.*, 1997) where it can be seen that the increase in the twist factor (Samples 7, 9 and 8) produces progressively more compact yarns. Yarns with a high level of twist are therefore more difficult to dye because closely packed fibres impede the removal of air trapped between the fibres and the penetration of dye solution into the yarn interior.

Yarn strength initially increases with the increase of the twist level due to the increasing frictional forces between the fibres. At the same time the contribution of fibre strength to the overall yarn strength decreases. As a result yarn strength reaches its maximum value at the critical twist (Fig. 2.8) after which point the strength tends to decrease. The thicker yarns are generally stronger and their critical twist is lower than for the finer yarns.

The twist level, which is necessary to achieve the best performance characteristics of the yarn, and the yarn count are linked via an additional parameter called twist factor:

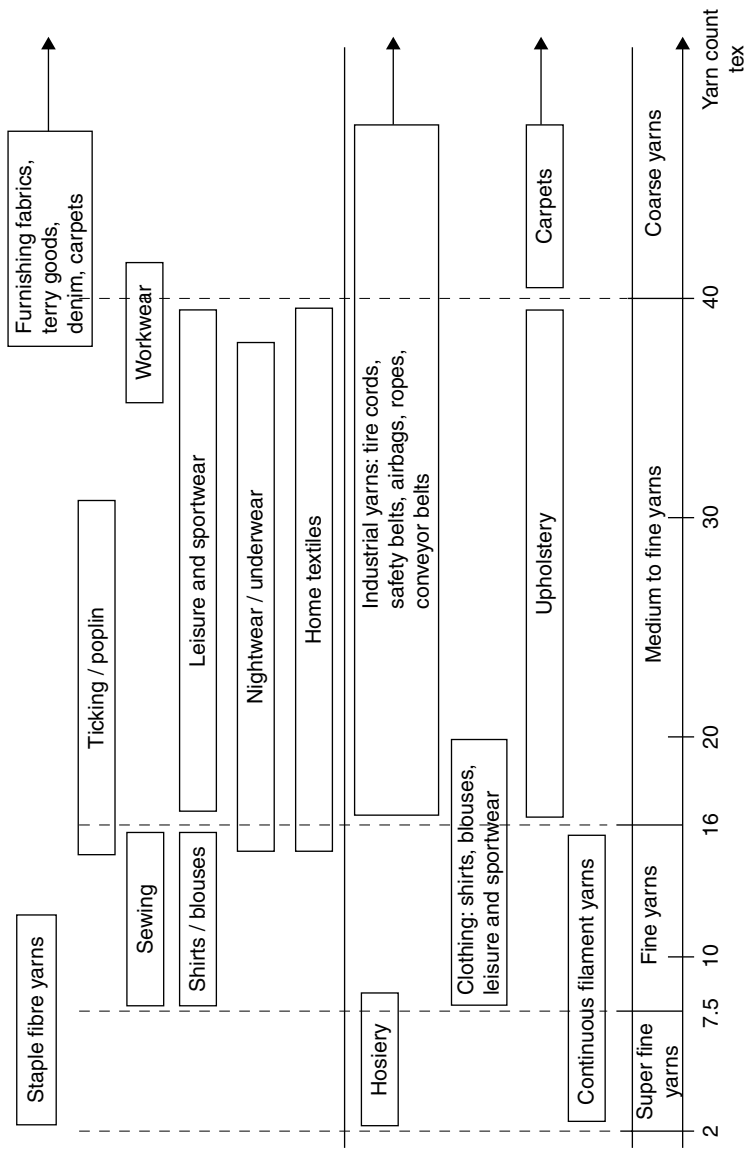
$$F = t \times \sqrt{T} \quad [2.4]$$

where

$F$  is the twist factor;

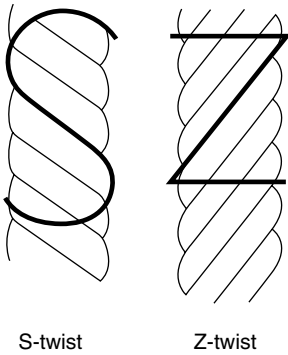
$t$  is the twist level;

$T$  is the yarn count in tex units.

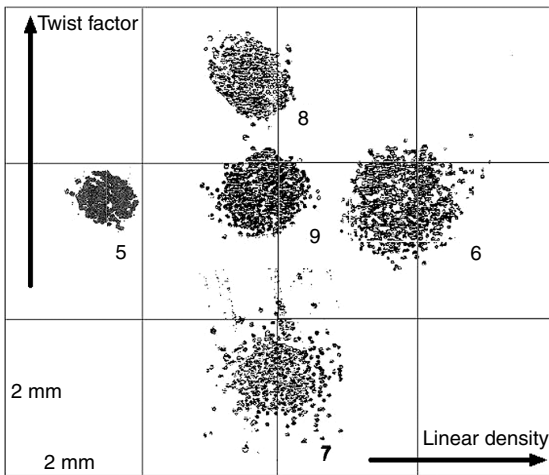


2.5 Yarn end-uses in relation to yarn count.

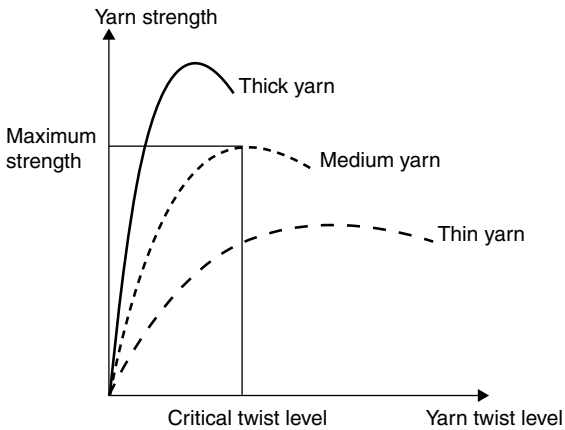




2.6 Yarn twist direction.



2.7 Effect of linear density and twist factor on fibre packing density.



2.8 Relationship between yarn twist level and strength.

**Table 2.3** Recommended yarn twist factors depending on spinning system and end-use

Spinning system	End-use	Twist factor
Cotton and blends with man-made fibres, staple length <25 mm	Warp yarns	3800–4800
	Weft yarns	3170–3650
Cotton and blends with man-made fibres, staple length <25 mm	Warp yarns	2400–2860
	Hosiery	2050–2550
Wool and blends with man-made fibres	Warp yarns	2050–2400
	Weft yarns	1750–2050
	Hosiery	1420–1750

*Source:* Adapted from Lawrence (2003).

Yarn twist factor is used to characterise the twist intensity for the yarns of various thicknesses (counts); twist factor ultimately defines the yarn end-use according to Table 2.3 (Lawrence, 2003). This ensures that the yarn is strong enough to withstand the action of external forces applied to the yarn in weaving and knitting and at the same time the yarn has a sufficient bulkiness and stability which are particularly important in knitting.

Yarns can be dyed in the form of hanks or conical/cylindrical packages. Before dyeing yarns must be scoured in order to remove grease, wax and any other natural or added substances which may be present on the surface of the fibres and make dyeing difficult. Hank dyeing is more expensive than package dyeing but can be employed for yarns used for knitting because this method produces yarns with greater evenness and voluminosity. Due care, however, should be taken in hank dyeing because relative movement of the yarns and dyeing liquor may damage the yarns which usually have lower twist level in comparison to yarns for weaving.

In package dyeing it is necessary to ensure that the volume density of the package is the same on its surface and in the core. The direction of flow of the dyeing liquor in package dyeing is usually alternated between exterior-to-interior and interior-to-exterior so that a uniform distribution of the dye is achieved throughout the package.

## 2.5 Physical chemistry of fibre polymers

The previous section discussed a combination of fibre properties which make it suitable for spinning and then for conversion into fabric. In a similar way there are certain properties that define fibre dyeability. Dyeability, however, is a very complex property which cannot be defined through a single parameter. For example, cotton can be dyed by direct dyes but not by the disperse dyes whereas polyester behaves in the opposite way. In this respect it is necessary to introduce the basic chemical and physical processes that accompany fibre dyeing at molecular level.

### 2.5.1 Phases of dyeing process

In general, dyeing can be described as a process in which a textile fibre absorbs the molecules of dye from its solution so that the dyed material retains the dye and resists the release of the dye back to the solution from which it has been absorbed. Dyeing processes which take place in water solutions of dyes are always distribution processes between two phases, i.e. dye solution and solid substrate, and they are based on physicochemical interactions between the molecules of dye and the substrate. These processes may be accompanied by chemical reactions between the dye molecules and the substrate, for example, in the case of vat, reactive and chrome dyes. In the case of disperse dyes, the second solid phase takes part in the process, that is the disperse particles of the dye. These particles dissolve in the water and thus the transport of the dye into the solid substrate takes place in a similar manner to that of water-soluble dyes. In contrast to these two cases, dyeing with pigments is based on the mechanical anchoring of the pigment particles on the surface of the substrate.

The dyeing process in water solutions can be divided into four stages as follows:

1. Convective diffusion of the dye in the dyebath during which individual dye molecules move within the liquid phase towards the fibre. This is a relatively fast process which can be accelerated by relative movement of the dye solution and fibre.
2. Absorption of the dye on the fibre surface where dye molecules pass from the liquid phase (dye solution) to the solid phase (fibre). Fibre surface here is understood not only as the outer visible surface of the fibre, which is defined by fibre diameter and fibre length, but also as the surface of pores which may penetrate deep into the fibre interior. This stage to a large extent defines the uniformity of colour of the end-use product.
3. Molecular diffusion of the dye from the fibre surface towards the fibre interior. This is a slow process the rate of which can be increased by raising the temperature of the dye solution. Higher temperature also helps in increasing fibre swelling.
4. Fixation of dye molecules on the fibre molecules by the formation of bonds between the molecules of dye and the fibre. The stability of fixation depends on the type of bond that has been formed.

### 2.5.2 Physical structure of polymers

Physical structure of fibre polymer is one of the main factors which affect fibre dyeing. The majority of textile fibres are natural or synthesised polymers.

A polymer can be defined as a large molecule (macro-molecule) composed of small repeating units (monomers) which are joined together by covalent chemical bonds. Polymer molecules may consist of many thousands or even millions of atoms which are arranged into regular, crystalline regions or irregular, amorphous structures. Atoms may be arranged into three-dimensional, two-dimensional or one-dimensional (linear, chain) molecules. The last type of arrangement forms the most important and numerous group of polymers which can be found in natural fibres and also used in the manufacture of man-made fibres.

There are three important characteristics related to the dimensions and orientation of linear polymers. Degree of polymerisation is the average number of repeating units in the individual macro-molecule of a polymer. For example, molecules of cellulose in cotton fibres typically consist of between 800 and 10 000 units (Klemm *et al.*, 2005). Molecular weight is the total of atomic weights of all atoms in the individual macro-molecule of a polymer; in general, greater molecular weight means larger macro-molecules. Degree of orientation shows to what extent the macro-molecules in a fibre lie in the same direction which is usually the fibre axis; increase in orientation leads to the increase of fibre strength but at the same time usually decreases the ability of fibre to stretch.

Many polymers contain carbon atoms in their repetitive units; these atoms may have their four bonds oriented in different ways making them either right-hand (R) or left-hand (L) asymmetrical. A linear polymer formed entirely by R-units or L-units is called an isotactic polymer. If R-units and L-units in polymer alternate in a regular manner it is called a syndiotactic polymer. In an atactic polymer R- and L-units are randomly arranged. The crystalline regions are formed from isotactic or syndiotactic polymers.

An important property of all fibre polymers used in textiles is glass transition temperature (GTT) usually denoted as  $T_g$ . The concept of GTT is applied only to non-crystalline regions. GTT can be defined as a critical temperature at which the material changes its behaviour from being hard and brittle (similar to glass) to elastic and flexible like rubber. This change in properties is explained by the change in the ability of molecules and atoms to move. At a temperature below  $T_g$  any large-scale motion is not possible whereas at a temperature above  $T_g$  molecules and atoms acquire sufficient energy which makes it possible for them to move on the scale of the repeating unit.

In order for the dyeing process to take place the molecules of dye should penetrate into the polymer structure. For this (i) the concentration of the dye on fibre surface must be higher than inside the fibre; (ii) the polymer structure should have spaces large enough for the dye molecules to move into the fibre interior or, alternatively, the dye molecules should be sufficiently small for this to happen and (iii) molecular chains of fibre polymer

should have sufficient freedom of movement in order to facilitate the movement of dye molecules.

The dependence of the flow of dye molecules on the gradient of concentration is given by Fick's law as follows:

$$J = -D \frac{\partial C}{\partial x} \quad [2.5]$$

where

$J$  is the flow of the dye molecules;

$D$  is the diffusion coefficient which characterises the rate of diffusion;

$C$  is dye concentration;

$x$  is distance.

The Stokes–Einstein equation gives an inverse proportion of the diffusion coefficient to the radius of particles:

$$D = \frac{RT}{6\pi\eta N_A} \frac{1}{r} \quad [2.6]$$

where

$R$  is gas constant;

$T$  is the absolute temperature;

$\eta$  is viscosity;

$N_A$  is Avogadro constant;

$r$  is the radius of the spherical particle.

Since the size of the dye molecule is proportional to its molecular weight it is preferable to have dyes of low molecular weight in order to increase the diffusion coefficient and thus to speed up the dyeing process.

The crystalline domains do not change when immersed in water meaning that it should be amorphous regions that are responsible for the diffusion of dye into the fibre. There are three models that describe this process.

The pore theory (Bae *et al.*, 1997; Brady, 1992; Chen *et al.*, 2001; Strnad *et al.*, 2003) is applicable to the polymer systems which do not display a high level of molecular chains movement over a temperature range but swell in water like cellulosic fibres. It is assumed that the pores in amorphous regions have a tendency to swell and significantly increase in size; they then are filled with water and provide a pathway for the dye molecules to move inside the fibre.

The free-volume theory (Bell, 1968; Vrentas and Duda, 1977; Vrentas and Vrentas, 2003; Zielinski and Duda, 1992) assumes that diffusion of the dye is not attributed to the swelling but to the increased mobility of molecular chains in amorphous regions at the temperatures above GTT ( $T_g$ ). Typical examples here are polyester and acrylic fibres.

According to the transition-state theory (Evans and Polanyi, 1935; Eyring, 1935; Laidler and King, 1983; Winzor and Jackson, 2006) the diffusion takes

place when a dye molecule gains an extra energy and passes from its equilibrium state to an activated (transition) state and then back to the equilibrium state but at a different location in the polymer structure.

It can be understood from the discussion above that the increase in degree of crystallinity, which is defined as a percentage of crystalline part in a unit mass of a polymer, decreases the rate of diffusion.

### 2.5.3 Intermolecular bonds

Intermolecular bonds play a critical role in providing necessary strength to the fibres and in fixation of dye molecules in the fibre structure. There are four types of bonds that can be formed between the monomers in the fibre polymers and between dye molecule and the molecule of the fibre polymer. Typically the strength of the bond is characterised by the energy of interactions between the atoms involved. This energy can be calculated using methods of quantum mechanics (Atkins, 1994) and usually is given in kJ per 1 mol, where 1 mol is the amount of substance that contains the same number of atoms or molecules as there are atoms in exactly 12 g of carbon-12,  $C^{12}$ . This number is known as Avogadro's constant,  $N_A = 6.02214179(30) \times 10^{23}$  (Mohr *et al.*, 2006).

1. Van der Waals bonds are formed due to the intermolecular forces between two chemically inert molecules. These include electrostatic attractive forces between polar molecules, dipoles of various natures and repulsive forces between the atomic nuclei. The van der Waals bonds are characterised by low energy of up to 8.5 kJ/mol (Balashova *et al.*, 1984). One of the examples of van der Waals bonds are those between carbon and nitrogen atom in the CN group of polyacrylonitrile (PAN).
2. Hydrogen bonds are formed by attractive interaction between a hydrogen atom, H and another two atoms in the form A–H...B, where A and B are electronegative atoms. There are three elements which form the most effective hydrogen bonds, i.e. N, O and F. The hydrogen bonds are stronger than the van der Waals interactions but weaker than both ionic and covalent bonds; typical values are given in Table 2.4 (Emsley, 1980; Markovitch and Agmon, 2007). Examples of hydrogen bonds in fibre polymers include (i) bonds between CO and NH groups in polyamide and protein fibres and (ii) between hydroxyl groups OH within and between neighbouring chains of cellulose molecules. The latter bonds facilitate the formation of microfibrils in cellulose fibres which define their strength.
3. Ionic bonds are formed as a result of a complete transfer of electrons between two atoms. This happens, for example, in the formation of NaCl

**Table 2.4** Energy of hydrogen bonds

Molecule	Energy (kJ/mol)
F—H...F	155
O—H...N	29
O—H...O	21
N—H...N	13
N—H...O	8

*Source:* Adapted from Emsley (1980); Markovitch and Agmon (2007).

**Table 2.5** Energy of covalent bonds (kJ/mol)

Diatomic molecules					
Molecule	Energy	Molecule	Energy	Molecule	Energy
H—H	436	H—O	428	H—F	565
O=O	497	C=O	1076	N≡N	945
Polyatomic molecules					
H—CH <sub>3</sub>	435	H—NH <sub>2</sub>	460	H—OH	492
H—C <sub>6</sub> H <sub>5</sub>	469	H <sub>3</sub> C—CH <sub>3</sub>	368	H <sub>2</sub> C=CH <sub>2</sub>	720
HC≡CH	962	O=CO	531	HO—OH	213

*Source:* Adapted from Atkins (1994).

when a sodium atom (Na) donates one electron to a chlorine (Cl) atom. The energy of ionic bonds can be calculated using the Born–Lande equation (Johnson, 2002) or Born–Haber cycle (Atkins, 1994). This energy in some typical salts is as follows: NaCl – 787 kJ/mol; KCl – 717 kJ/mol; CaCl – 2255 kJ/mol (Atkins, 1994).

- Covalent bonds are formed between two neighbouring atoms sharing a pair of electrons like, for example, in the molecule of hydrogen H<sub>2</sub>. These bonds can be non-polar in the case of equally shared electrons (Cl<sub>2</sub>), or polar if the electrons are shared unequally (HCl). There are two theories describing the formation of covalent bonds. The valence-bond theory assumes that the bond is formed by two overlapping atomic orbitals of two atoms each containing one unpaired electron whereas the molecular orbital theory does not consider the shared electrons as belonging to any individual atom but rather distributed in molecular orbitals over the entire molecule. The covalent bonds are the strongest of the bonds mentioned; the energy of covalent bonds is presented in Table 2.5 (Atkins, 1994). For example, covalent bonds in C–C and C–N groups of wool keratin are characterised by bond energy of 347 kJ/mol and 291 kJ/mol, respectively (Feughelman, 1997).

It can be seen that the critical issues in the dyeing process are the molecular structure of both the fibre and the dye together with the energy relationships of the whole system which includes water or any other solvent used in the dyeing process.

### 2.5.4 Fibre wettability

One of the major factors affecting dyeability of a fibre is its wettability since dyeing normally takes place in water solutions of dyes. The fibre thus must have a wettable surface.

If a small droplet of water is placed on the fibre surface it will spread over the surface to some extent and assume a shape depending on the surface forces acting along the common boundary line between three phases: solid phase of the fibre, liquid phase of water and surrounding air. The shape of the droplet can be characterised by an angle measured between the tangent to the curved surface of the droplet and the surface of the solid fibre (Fig. 2.9). This angle  $\theta$  is called the contact angle and can be expressed through the surface free energies (or surface tensions) by Young–Dupre equation as follows:

$$\gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta \quad [2.7]$$

where

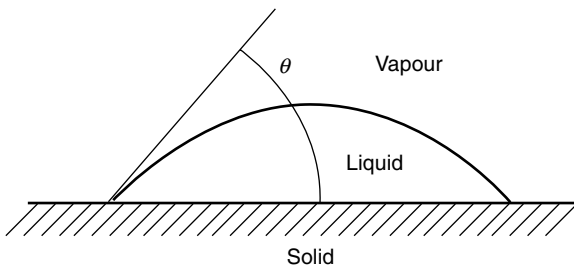
$\gamma_{SA}$  is the surface tension of solid against air;

$\gamma_{SL}$  is the surface tension of solid against liquid;

$\gamma_{LA}$  is the surface tension of liquid against air.

If the contact angle  $\theta = 0^\circ$  then the surface is completely wettable and non-wettable if  $\theta = 180^\circ$ .

Equation [2.7] is applicable to the case when the surface of the solid phase is perfectly smooth, flat, rigid and chemically homogeneous. The theoretical



2.9 Contact angle.



treatment of various more realistic scenarios can be found in Good (1992), Marmur (2003) and Whyman (2008).

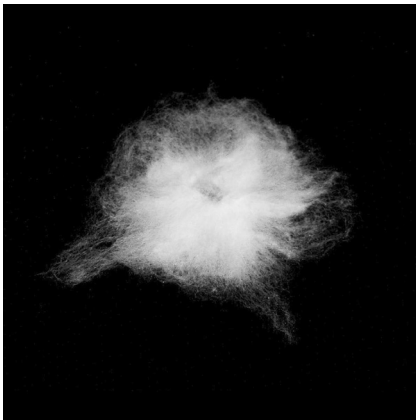
## 2.6 Cellulosic fibres

There are many natural cellulosic fibres that can be obtained from different parts of plants such as seeds (cotton), leaves (manila, sisal), husk of coconuts (coir) and stems where examples include flax, hemp, jute and ramie which are often referred to as bast fibre crops. This section will concentrate on the properties of cotton fibre.

### 2.6.1 Properties of cotton fibre

Cotton fibre is one of the most important natural textile fibres of plant origin and accounts for about one third of the total world production of textile fibres. Cotton fibres grow on the surface of the seed of cotton plant (Fig. 2.10). Cotton fibre contains 90–95% cellulose which is an organic compound with the general formula  $(C_6H_{10}O_5)_n$ . Cotton fibres also contain waxes, pectins, organic acids and inorganic substances which produce ash when fibre is burnt.

Cellulose is a linear polymer of 1,4- $\beta$ -D-glucose units linked together by valence bonds between the carbon atoms number 1 of one glucose molecule and number 4 of another molecule. The degree of polymerisation of cellulose molecule may be as high as 10 000 (Klemm *et al.*, 2005). The hydroxyl groups OH protruding from the sides of the molecule chain link neighbouring chains together by hydrogen bond and form ribbon-like microfibrils which are further arranged into larger building blocks of the fibre.



2.10 Cotton fibres on cotton seed.

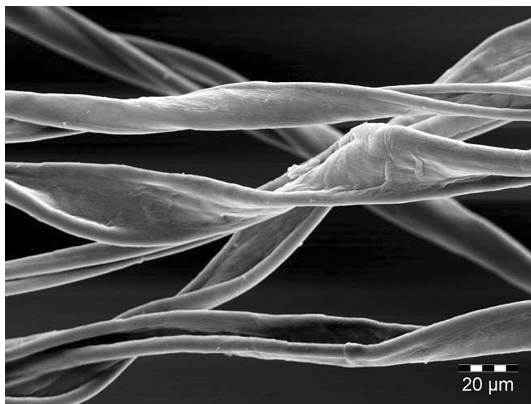
Cotton fibre is partly crystalline and partly amorphous; the degree of crystallinity measured by X-ray methods is between 70 and 80%.

The cross-section of cotton fibre resembles a 'kidney bean' shape where several layers can be recognised as follows:

1. The outermost cell wall which in turn is composed of the cuticle and the primary wall. The cuticle is a thin layer of waxes and pectins which covers the primary wall consisting of microfibrils of cellulose. These microfibrils are arranged into a network of spirals with right- and left-hand orientation.
2. The secondary wall is composed of several concentric layers of microfibrils which periodically change their angular orientation with respect to the fibre axis.
3. The collapsed central hollow is lumen consisting of dried remains of cell nucleus and protoplasm.

In longitudinal view cotton fibre is readily recognisable by its characteristic twisted structure (Fig. 2.11).

Properties of cotton fibre can have large variations depending on the botanical group of the plant from which the fibre is obtained, the soil in which the plant is cultivated, climate and weather conditions, farming practices and many other factors. Fibre length which can be obtained from the seeds ranges from 3 to 63 mm. Fibres that are shorter than 12 mm are not considered suitable for spinning and therefore have no commercial value for the textile industry. The characteristic of fibre length which is used in the industry is called the staple length; this is the length of the most frequently occurring fibres. Typical staple length



2.11 Longitudinal view of cotton fibres (courtesy of the *Journal of the International Forum for Cotton Promotion*).

of Indian and Asian cottons (*Gossypium herbaceum* and *Gossypium arboreum*) is 9.5–25 mm, for American Upland cottons (*Gossypium hirsutum*) 19–35 mm, for Egyptian-type cottons (*Gossypium barbadense*), which are also known as South-American and Extra Long Staple cottons, 38–63 mm. The longest cottons, however, account for only some 5% of all cotton produced; the majority of fibres used in the industry are from 20 to 32 mm long.

The fineness of cotton fibre can be defined (i) by its linear density, which is typically between 0.13 and 0.21 tex, (ii) by Micronaire reading measured by airflow instruments with typical range between 2.0 and 6.5 and (iii) despite the fibre's non-circular cross-section, by its diameter which is estimated to be between 12 and 20  $\mu\text{m}$ .

Individual cotton fibres can show tensile strength of up to 5 cN and breaking elongation up to 10% but the usual characteristic of strength is tenacity; this is the ratio of the tensile strength to the linear density. In dry conditions the tenacity of cotton fibres is 25–45 cN/tex; in wet conditions cotton fibres become 10–20% stronger.

At standard atmospheric conditions (65% relative humidity and 20°C) the moisture regain for cotton is 7.5% on average.

Cotton fibre is resistant to alkalis and bleaching materials but can be easily damaged by strong concentrated acids such as hydrochloric and sulphuric acids and strong oxidisers such as potassium permanganate and sodium hypochlorite.

Cotton can be dyed with direct dyes, diazotable dyes, oxidation dyes, vat dyes and reactive dyes.

## 2.7 Protein fibres

This section considers structure and properties of two natural fibres of animal origin, i.e. wool and silk fibres.

### 2.7.1 Properties of wool fibre

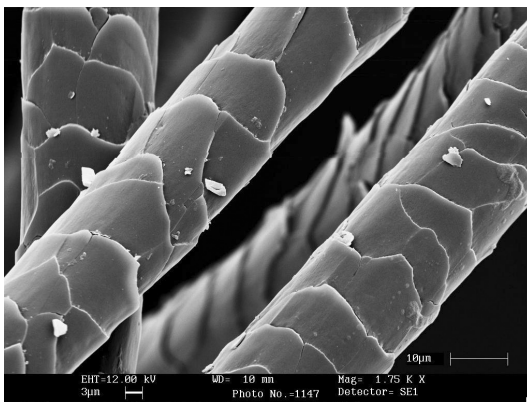
Wool is the natural protein-based staple fibre that grows on the body of sheep. The chemical composition and internal structure of wool are highly complex. The main proportion of the fibre material is  $\alpha$ -keratin which is a biological polymer formed by polypeptide chains composed of amino acids such as cystine, lysine, arginine, glutamine and others (Lewis, 1992). Molecules in the polypeptide chain are joined together by a covalent bond which is formed between the carboxyl group COOH of one molecule and the amine group  $\text{NH}_2$  of the other molecule resulting in a functional group CONH which is called a peptide link.

Structurally wool fibre consists of outer layer called cuticle, the main body called cortex, and, in some fibres, the central cavity called medulla. The cuticle is a layer of flat slightly overlapping scales (Fig. 2.12); the thickness of the scales is between 0.2 and 0.4  $\mu\text{m}$ , they are 30–50  $\mu\text{m}$  wide and 16  $\mu\text{m}$  long (Makinson, 1979; Swift, 1977). The cortex, which constitutes some 90% of the wool fibre, consists of cortical cells about 500  $\mu\text{m}$  long and 5  $\mu\text{m}$  thick. The cells are formed by macrofibrils of about 0.5  $\mu\text{m}$  in diameter which in turn are groups of microfibrils of 7.3 nm in diameter (Spei and Zahn, 1979) embedded into a matrix. Microfibrils consist predominantly of low-sulphur proteins whereas the matrix is made from high-sulphur proteins (Bendit, 1968). Individual microfibrils have a left-handed coiled-coil structure where pairs of right-handed  $\alpha$ -helical units of keratin molecules can be identified by X-ray diffraction (Fraser *et al.*, 1972; Fraser and MacRae, 1973).

Wool fibre cross-section is slightly elliptical but usually the cross-sectional dimension is estimated by the fibre diameter which can be from less than 15.5  $\mu\text{m}$  for ultrafine Merino wool to more than 70  $\mu\text{m}$  for coarse carpet wools (AWEX, 2010; Lawrence, 2003).

Wool fibre length varies depending on the breed and can be from 35 to 350 mm. The length of Merino wool normally used in industrial practice ranges from 60 to 110 mm whereas coarser carpet wools are from 100 to 200 mm long (Postle *et al.*, 1988).

Wool fibres display sufficient tensile strength (tenacity is in the range of 15–20 cN/tex) and very good elasticity. Wool fibre can return to its original length after 30% elongation; breaking elongation of wool fibre is up to 35% in dry conditions and 45% when wet. The strength of wool diminishes by 10–20% in wet conditions.



2.12 Longitudinal view of wool fibre ([http://www.biotechlearn.org.nz/focus\\_stories/wool\\_innovations/images/longitudinal\\_view\\_of\\_synthetic\\_fibre\\_and\\_wool\\_fibre](http://www.biotechlearn.org.nz/focus_stories/wool_innovations/images/longitudinal_view_of_synthetic_fibre_and_wool_fibre)).

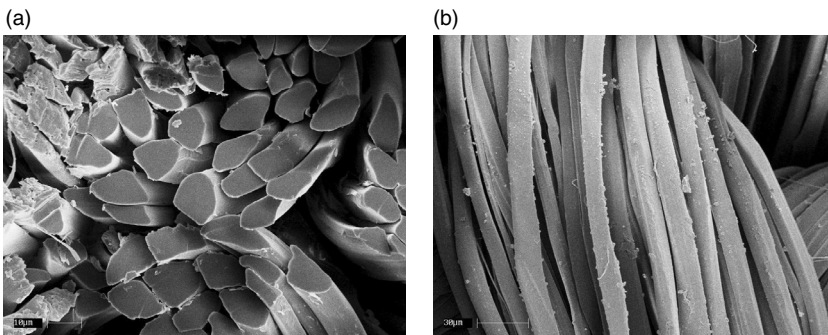
Wool fibre absorbs moisture well and can retain an amount of water of up to 30% of its dry weight; this property makes wool easy to dye.

Wool fibre has good insulation properties which are characterised by low thermal conductivity of 54 mW/m<sup>2</sup>/K (Morton and Hearle, 2008).

Alkali treatments damage wool structure making it less strong and causing yellowness. At the same time wool is resistant to dilute acids; this is used for removing vegetable impurities from wool by treating wool fibre with 6% solution of sulphuric acid. Concentrated sulphuric and nitric acids, however, can disintegrate the wool structure. Wool can be dyed by direct dyes, reactive dyes, acid dyes and metal-complex dyes.

## 2.7.2 Properties of silk fibre

Silk is a protein-based fibre produced as a continuous filament by the larvae from a variety of insects and spiders. The most widely used and useful silks are produced by the larvae of the domesticated moth *Bombyx mori* which are commonly called mulberry silkworm because the caterpillar feeds on mulberry leaves. Silkworm produces silk in the form of two filaments consisting of fibroin and glued together by the protein gum sericin (Fig. 2.13). Chemically fibroin consists of many amino acids linked together to highly crystalline and uniformly oriented chains lying parallel to the fibre axis. Silk fibroin is characterised by the high content of glycine, alanine, serine and tyrosine which together account for up to 85% of the total residues (Lucas, 1966; Zhan *et al.*, 1967). Molecular weight of fibroin has been estimated to be in the range of 350 000–370 000 daltons (Tashiro and Otsuki, 1970; Sprague, 1975). Sericin is a hydrophilic protein which is explained by the difference in its chemical composition from fibroin; in sericin some two-thirds of residues are serine, aspartic acid and glycine. The molecular weight of sericin is in the



2.13 Cross-sectional (a) and longitudinal (b) views of silk fibres (courtesy of Dr Jinsong Shen, TEAM Research Group, De Montfort University, Leicester, UK).



2.14 Silk cocoon.

range from 20 000 to 200 000 Da (Sprague, 1975). The hydrophilic nature of sericin makes it easy to separate two silk filaments by degumming in boiling water and then to unwind the cocoon (Fig. 2.14) to obtain raw silk where individual filaments may be more than 2000 m long.

At macro-molecular level fibroin consists of polypeptide chains which are linked by hydrogen bonds between the CO and NH groups.

The cross-section of individual silk filaments is triangular or elliptical. In practice, however, the thickness of silk filaments is characterised by its average diameter which ranges from 15 to 25  $\mu\text{m}$  or by the linear density which is between 0.19 and 0.44 tex.

Silk is a valuable natural fibre due to its high strength (tenacity 38 cN/tex) and breaking elongation (27.2%) (Meredith, 1945), excellent handle and drape qualities.

Similar to wool, silk can be dyed with acid dyes, metal-complex dyes, reactive dyes and direct dyes.

## 2.8 Man-made fibres

Man-made fibres constitute what in modern times have become a large and important class of fibres widely used in the manufacture of textiles. Man-made fibres are composed of polymers which may (like cellulose) or may not (like polyamide) occur naturally.

Despite large differences in the chemical composition and properties of man-made fibres their production follows three general stages as follows (Mark *et al.*, 1967):

1. Preparation of spinning fluid from either solid polymer or directly from monomers.

2. Fibre spinning by means of extrusion of the spinning liquid through a number of small holes in a spinneret (Fig. 2.4) followed by solidification of the emerging jets into continuous filaments.
3. Mechanical, thermal and chemical after-treatment of the fibres to improve their properties.

The amount of published research and the number of patents covering industrial aspects of man-made fibre properties and production methods is truly immense. This section presents some basic information on structure, properties and production processes of typical man-made fibres such as viscose, polyester, nylon and acrylic.

### 2.8.1 Viscose fibre

Viscose fibre is an example of a regenerated fibre which is the fibre produced by rearrangement of the molecules of natural cellulose obtained from wood pulp. The production process for viscose consists of several stages as follows:

1. Immersion – The wood pulp from spruce or pine trees is immersed in 18% solution of sodium hydroxide (NaOH) at a temperature of about 25°C to produce sodium cellulose (C<sub>6</sub>H<sub>9</sub>O<sub>4</sub>ONa)<sub>n</sub> in the form of a sheet material.
2. Pressing and shredding – The excess liquid is removed by pressing the sheets between rollers which then are shredded into a loose mass called ‘white crumb’.
3. Aging – White crumb is depolymerised by oxidation and hydrolysis (Dyer and Phifer, 1971) to control the viscosity of the liquid.
4. Xanthation – The aged material is treated with carbon disulfide (CS<sub>2</sub>) at a controlled temperature of 20–30°C to form cellulose xanthate (C<sub>6</sub>H<sub>9</sub>O<sub>4</sub>OCS<sub>2</sub>Na)<sub>n</sub> called ‘yellow crumb’.
5. Ripening – Xanthation is a reversible reaction. Cellulose xanthate decomposes into free CS<sub>2</sub> and cellulosic hydroxyls forming a viscose gel which is dissolved in a dilute solution of NaOH.
6. Filtering and deaeration – The viscose is filtered to remove any undissolved particles and pressed to remove air bubbles.
7. Extruding – The viscose solution is extruded through a spinneret (Fig. 2.4).
8. Spinning – Jets of viscose emerging from the spinneret are passed through a bath of sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), resulting in the formation of solidified continuous filaments which are also known as viscose rayon. The filaments are then drawn to increase the degree of molecular chains alignment and orientation thus increasing their strength and washed to remove any residual chemicals.

The structure of the viscose fibre filaments is different at the surface and in the core, i.e. near the surface the structure consists of many small crystalline regions whereas at the core they are fewer but larger.

The longitudinal view of viscose fibres shows characteristic lines running down the length of the fibre. The cross-section of the fibre may have an irregular shape which is explained by the difference in the rate of polymerisation at different areas of the cross-section. Viscose fibres may be produced having round, flat and trilobal cross-sections.

Viscose staple fibres are produced in a variety of linear densities ranging from 0.17 to 0.88 tex and lengths from 38 to 120 mm to suit the characteristics of other commonly used textile fibres such as cotton (<http://www.fibre2-fashion.com/sniace/products.asp>).

The mechanical properties of viscose fibres can be controlled by the manufacturing parameters. The fibres which are in common use for apparel production have a relatively low tenacity of 18 cN/tex and high extensibility of 27.2% whereas high modulus high tenacity fibres used in technical textiles are more than twice as strong at 41 cN/tex but less extensible having breaking extension of 12% (Morton and Hearle, 2008).

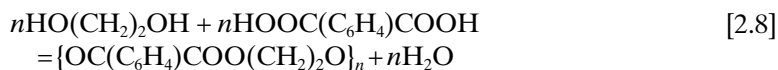
Viscose fibres, despite their similarity to cotton in terms of chemical composition, behave differently in wet conditions, i.e. normal viscose fibres are more than 50% stretchable in wet conditions but display only half of their strength in comparison to dry conditions.

Normal viscose fibres can retain water of up to 100% of their own weight whereas super-absorbent fibres produced with the addition of water-holding polymers such as sodium carboxymethylcellulose retain up to 200% of their weight in water.

Fabrics made from viscose fibres are generally soft, comfortable in hot and humid conditions, drape well, highly absorbent and easy to dye. On the other hand, viscose fabrics have low dimensional stability in repeated washing, are prone to creasing, and tend to stretch.

## 2.8.2 Polyester fibre

Polyester fibre is an example from the large group of 'truly' man-made fibres since they are produced from synthesised polymers which do not exist in nature. There are many different types of polyester but all of them are produced by condensation reaction and they all contain ester functional group COO. The most important type of polyester is poly(ethylene terephthalate) (PET), commonly referred to simply as polyester. This is the product of condensation reaction between ethylene diglycol and terephthalic acid as follows:





This reaction is carried out at temperature reaching 290°C and a pressure of 400 kPa.

Polyester is a thermoplastic polymer which can be re-melted and re-moulded. This property is used in the production and recycling of polyester fibres. Typically polyester fibres are produced as continuous filaments either from a granulated polymer (batch process) or by a continuous polymerisation. In the batch process granules are first dried at a temperature of about 170°C in order to reduce the moisture content and thus prevent the hydrolysis of the polymer which leads to the deterioration of its properties. The granules are then melted and extruded through a spinneret at a temperature between 265 and 290°C. This process is often referred to as melt-spinning; the production speed may be as high as 4000 m/min. The emerging jets of polymer are immediately solidified by the flow of cool air. They are then drawn at a temperature above  $T_g$  (69°C) to improve the orientation of polymer chains and increase strength.

The structure of polyester fibres is a combination of crystalline and non-crystalline regions.

The tensile properties of polyester fibres vary depending on the parameters of the manufacturing process. Similar to other man-made fibres polyester can be produced with a variety of characteristics: for example, high tenacity and low extensibility (85 cN/tex and 7%, respectively) or with low tenacity and high extensibility (26 cN/tex and 40%, respectively) (Lewin and Pearce, 1985).

Polyester fibres can be produced as staple fibres suitable for blending with cotton in the range of linear densities of 0.13–0.33 tex and average lengths from 38 to 60 mm or for processing on worsted/woollen systems at linear density in the range 0.33–0.67 tex and length 80–100 mm.

Polyester fibres are characterised by low moisture absorption, an ability to accumulate electrostatic charges on the surface, and tendency to the formation of entangled bundles of fibres on the fabric surface (pilling effect).

Polyester fibres are resistant to the action of dilute acids, alkalis and organic solvents but can be badly damaged at high concentrations.

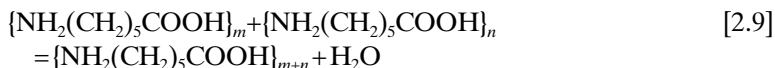
Due to the highly crystalline and dense structure and the presence of benzene rings which provide rigidity to the amorphous regions polyester fibres should be dyed at high temperatures of up to 140°C and elevated pressures. Usually polyester fibres are dyed with disperse dyes; some vat dyes of low molecular weight and azo dyes can be used as well.

### 2.8.3 Nylon fibre

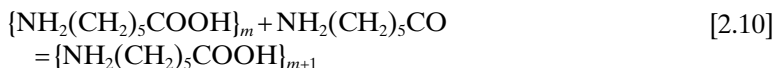
Nylon is the generic name for polyamide polymers which are linear polymers with structural units linked by amide functional group  $\text{NHCO}$ . Depending on

the chemical composition of the elementary units nylon fibres are denoted as Nylon X or Nylon Y, Z, where X is the number of carbon atoms in the amino acid, and Y and Z are the number of carbon atoms in the diamine and dicarboxyl acids, respectively. The most commercially important types are Nylon 6 and Nylon 6,6.

Nylon 6 is synthesised from aminocaproic acid by either polycondensation reaction as follows:

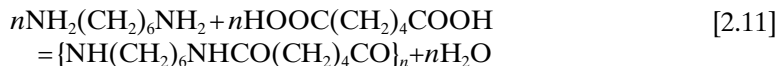


or by polyaddition:



Reaction usually takes place in an inert atmosphere of nitrogen at an elevated temperature of about 260°C. The resultant polymer consists of amide groups oriented in the same direction. Nylon 6 has a high molecular weight in the range from 14 000 to 20 000; GTT is  $T_g = 47^\circ\text{C}$ , and melting temperature  $T_m = 215^\circ\text{C}$  (Mark *et al.*, 1968).

Nylon 6,6 is synthesised by the condensation reaction as follows:



Nylon 6,6 has a high molecular weight exceeding 10 000, GTT  $T_g = 50^\circ\text{C}$ , and melting temperature  $T_m = 265^\circ\text{C}$  (Beaman, 1952). Dissimilar to Nylon 6 each two amide bonds in Nylon 6,6 are oriented in opposite direction.

Similar to many synthetic polymers nylon is partly crystalline and partly amorphous. Neighbouring macro-molecular chains of nylon are linked both by van der Waals forces and hydrogen bonds between NH and CO groups. This facilitates the formation of multi-folded molecular chains arranged in crystalline sheet-like agglomerates, which are some 6–10 nm in thickness, and fibrillar aggregates. These crystalline parts are often incorporated into spherical aggregates which are called spherulites; these are aggregates of molecules having dimensions large enough (up to 0.1  $\mu\text{m}$ ) to be recognised under the optical microscope (Hearle and Peters, 1963).

Nylon is a thermoplastic fibre and therefore it is produced by a melt-spinning process as a continuous filament followed by fibre drawing aimed at the improvement of mechanical properties. Properties of Nylon 6 and Nylon 6,6 quoted in the literature may vary depending on the exact conditions of manufacture such as draw ratio, rate of drawing and temperature applied,

but typical tenacity and elongation at break for Nylon 6 are 29 cN tex and 46%, respectively; for Nylon 6,6 tenacity may be in the range 37–66 cN/tex and breaking elongation from 16 to 43% with a negative correlation between these two parameters (Morton and Hearle, 2008). Both Nylon 6 and Nylon 6,6 display a significant degree of viscoelastic properties (Panga and Fancey, 2006; Selden and Dartman, 1998) which become more prominent with an increase of temperature.

Nylon fibres can be set by steaming or by dry heat; this treatment improves dimensional stability, wear and resistance to repeated washing.

Nylon 6 can be easily dyed by acidic, dispersed, chrome and vat dyes due to the hydrophilic groups present in the molecule chains. Nylon 6,6 can be dyed by dispersion as well as acid dyes.

#### 2.8.4 Acrylic fibre

Acrylic fibres are synthetic fibres based on linear polymer PAN; the building block of this polymer is a monomer with the formula  $\text{CH}_2\text{CHCN}$ . Conventionally fibres made with more than 85% of acrylonitrile are called acrylic fibres whereas if the content of acrylonitrile is between 35 and 85% then such fibres are called modacrylic. There are several industrial methods of producing acrylic fibres; many of them use hydrogen cyanide, HCN, which is a highly volatile liquid and high temperatures reaching 600°C. There are other methods based on reaction of propylene  $\text{CH}_3\text{CHCH}_2$  with ammonia  $\text{NH}_3$  or with nitrogen monoxide NO but they also require high temperatures which contribute to a high energy consumption of these methods.

The PAN fibres can be spun by wet-spinning method from the solutions of PAN in organic solvents, such as dimethylacetamide and dimethyl sulfoxide, or in concentrated solutions of metallic salts. The solidification of filaments coming from the spinneret takes place in water, alcohols or salt solutions in a spinning bath. In the dry-spinning method the filaments are solidified in hot air (Mark *et al.*, 1968). The filaments are then washed to remove the solvents and drawn in order to obtain fibres with the oriented molecular chains and improved mechanical properties. It is also possible to spin PAN fibres by melt-spinning method which requires the use of plasticisers in order to reduce the high melting temperature of the polymer which is 317°C.

The spinning method has a significant effect on the structure of PAN fibres. Fibres produced by the wet method are very porous containing a large number of microvoids of 0.1–1  $\mu\text{m}$  in size and characterised by a low density between 0.4 and 0.5  $\text{g}/\text{cm}^3$ . The density of the dry-spun fibres, ranging from 0.8 to 1.17  $\text{g}/\text{cm}^3$ , is close to the density of the polymer itself which is 1.17  $\text{g}/\text{cm}^3$ .

PAN fibres are produced in a variety of linear densities from 0.13 tex for textile applications to 0.67 tex for technical application and to 1.67 tex for

carpets. The latter fibres are often produced with a trilobal cross-section to achieve greater stiffness which is important in this application.

The mechanical strength of PAN fibres varies depending on the spinning method and finishing operations applied. Typically the tenacity of PAN is from 19 to 32 cN/tex and elongation at break is from 33 to 64% where higher tenacity corresponds to lower breaking elongation (Mark *et al.*, 1964).

Acrylic fibres have many useful properties such as durability and wear resistance, strong resistance to sunlight, resistance to all biological and many chemical agents such as diluted acids and alkalis, organic solvents, and to oxidation. Acrylic fibres are less flammable than cotton but more flammable than polyester and wool. The high content of carbon (67.9%) makes acrylic fibres highly preferable for the use as precursor for the production of carbon fibres with the yield of 50–55% (Morgan, 2005).

Acrylic fibres can be dyed with cationic dyes, anionic dyes or disperse dyes.

## 2.9 Sources of further information and advice

The bulk of knowledge on fibre structure and properties continues to grow with advances in fibre science and technology. The latest information on specific aspects of individual fibre types and polymers, both natural and man-made, can be found in papers published in general textile journals and in the journals dedicated to the study of specific fibres/polymers, as well as conference proceedings. Handbooks and general academic publications provide a wide range of summarised and critically evaluated information obtained from a number of different sources. The following list points to several valuable sources.

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#### Cellulose

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*Journal of Material Science*  
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*Textile Research Journal*

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## Pre-treatment and preparation of textile materials prior to dyeing

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**Abstract:** The chapter discusses various pre-treatments of textile materials to be carried out before dyeing, printing and finishing. The steps to be followed for white textile goods are also discussed. The variation in the pre-treatment methods for various textile fibres namely cotton, jute, flax, wool, silk and synthetic fibres are explained.

**Key words:** singeing, shearing and cropping, scouring, bleaching, fluorescent brightening agents, mercerisation, enzyme treatments.

### 3.1 Introduction

Textile materials possess a variety of impurities in grey state or immediately after manufacturing. Natural fibres (cotton, flax, wool, silk, etc.) have inherited natural impurities. In addition, oils, sizes and other foreign matter are added for improved spinnability (in yarn manufacture) or weavability (in fabric manufacture). Textile materials are also occasionally contaminated accidentally by impurities acquired during production. All such impurities or foreign matter are to be removed from textile materials for better coloration (dyeing or printing) or to make them marketable in white form. Such steps, called preparatory processes, depend mainly on two factors namely:

1. The type, nature and location of the impurities present in the fibre to be processed.
2. The fibre properties such as alkali-acid sensitivities, resistance to various chemicals, etc.

Preparatory processes may be broadly classified into two groups, namely:

1. Cleaning processes, where bulk of the foreign matter or impurities are removed by physical or chemical means.
2. Whitening processes, in which trace colouring matter is destroyed chemically or the whiteness of the materials is improved optically.



## 3.2 Impurities in textile fibres

The type and nature of impurities present in textile fibres depend on the source of origin. Natural fibres contain large quantities of various impurities. Man-made fibres are comparatively cleaner and contain insignificant quantities of impurities.

### 3.2.1 Impurities in vegetable fibres

Vegetable fibres contain varying types and quantities of impurities such as:

#### *Hemicellulose*

Hemicellulose is a substance with the general properties of carbohydrates and is a mixture of a variety of compounds, the proportions of which vary according to the source of origin. It is soluble in 18% caustic soda solution and this suggests that it may have a much lower degree of polymerisation than cellulose.

#### *Pectic acid and pectin*

Pectic acid occurs in vegetables as calcium, magnesium salt or as pectin (i.e. methyl pectate). Pectic acid is a long chain polymer similar to polysaccharide having one carboxyl group (instead of  $\text{CH}_2\text{OH}$ ) for every sixth carbon atom. It consists of a polygalacturonic acid backbone, which may be partially methylated and often has rhamnose, arabinose, galactose and xylose and other sugar bonded on as side chains. It is insoluble in water, but soluble in alkaline solutions.

#### *Lignin*

This substance is absent in cotton, but occurs in considerable amounts in bast fibres and is responsible for their yellowing. It is associated with woody tissues in plants as cementing material. Its constitution is not well established; its low hydrogen content in relation to carbon suggests that it may be composed of aromatic nuclei. 3,4 dihydroxyphenylpropane is a degradation derivative and is probably one of its basic structural units. It is soluble in sodium hypochlorite or sodium chlorite solution.

#### *Fats and waxes*

The fats and waxes are present in the fibres in much lower quantities. The oils can be made water-soluble by saponification, but the waxes are not saponifiable. Waxes are the product of monohydric alcohols (ceryl alcohol, gossypyl

alcohol, montanyl alcohol, etc.). They can be emulsified and removed with soap at high temperature. The melting points of cotton waxes vary between 68 and 80°C.

#### *Nitrogenous compounds*

These are degradation products of protoplasm contained in the living cells of plants. These protein and polypeptides substances are present in cotton in small amounts. They may produce undesirable effects in finished materials. They are readily soluble in boiling alkali.

#### *Minerals*

The quantity and composition of water-soluble mineral matter vary according to the nature of the soil on which cotton is cultivated. Silicon is always present. The metallic salts commonly present are of iron, aluminium, calcium and magnesium. The salts are converted into respective carbonates when burnt.

#### *Natural colouring matters*

The yellow or brown colour of cotton still remains even after scouring. These natural colouring matters can be effectively destroyed or made colourless by oxidising bleaching agents. They are present in traces and are probably related to the flavone pigments of cotton flowers.

The tentative compositions of various vegetable fibres are shown in Table 3.1.

### 3.2.2 Impurities in protein fibres

The keratin in natural wool is heavily contaminated with impurities to the extent of 30–70%. The average compositions of Australian Merino and

*Table 3.1* Chemical constituents of vegetable fibres (% on dry wt.)

Constituent	Matured cotton	Flax	Jute	Ramie
$\alpha$ -Cellulose	88–96.5	70.3	69.7	79.1
Hemicellulose	–	18.6	13.3	14.6
Pectin	0.4–1.2	2.0	0.2	2.1
Lignin	–	2.2	13.1	0.66
Fat and wax	0.4–1.2	2.6	0.5	0.3
Nitrogenous compounds	1–1.9	2.8	1.6	2.1
Ash (inorganic salts)	0.7–1.6	1.5	1.6	1.1
Others	1.7	–	–	–

**Table 3.2** Average composition (%) of raw wool fibres

Ingredient	Merino	Cross-bred
Fibre	49	61
Dirt	19 (6.3–43.8)	8 (7.9*)
Suint	6 (2–12)	8 (2.2–12.1)
Grease	16 (10–25.4)	11 (1.6–8.5)
Water	10	12

Bracketed values are minimum-maximum (\* average) values for different lots (Simpson and Crawshaw, 2002)  
*Source:* Adapted from Trotman (1968).

**Table 3.3** Illustrative compositions of wool fibres with varying diameter

Diameter ( $\mu\text{m}$ ) $\rightarrow$	23	23	28	35	45
Yield (%)	63	54	72	75	87
Clean dry fibre (%)	54	45	63	66	76
Water (%)	10	10	11	12	12
Grease (%)	15	8	9	5	5
Suint (%)	5	4	12	10	7
Dirt (%)	15	30	4	7	–
VM (%)	1	3	1	–	–

*Source:* Lewin and Sello, (1983)

cross-bred fleeces are shown in Table 3.2 (Simpson and Crawshaw, 2002; Trotman, 1968).

The compositions vary with the fineness of wool fibre. Table 3.3 illustrates the composition of typical wool fibres of different fibre diameters. The lower yield obtained from other varieties of wool with the same diameter may arise from the presence of extra dirt or vegetable matter (VM) (Lewin and Sello, 1983).

Adventitious dirt is inherently adhered with wool fibre. This is held by the adhesive action of the grease and falls away when the latter is removed during scouring. Fragments of vegetable substance are also picked up by sheep from various sources. These may be particles of straw, seed, burr or bast fibre.

Suint is a complex mixture derived from the sweat of the animal. It contains potassium salts of fatty acids, such as oleic and stearic acids. The simple organic acids such as acetic, lactic, butyric and valeric acids are also found in the free-state as well as potassium salts. Amino acids like leucine, glycine and tyrosine are detected. These are soluble in water and can be isolated from the raw wool by aqueous extraction.

Wool wax is derived from fatty acids and complex monohydric alcohols. The number of wool wax acids may be as high as 138, predominantly

consisting of alkanolic,  $\alpha$ -hydroxy- and  $\omega$ -hydroxy-acids. Each group contains normal, iso (having a terminal isopropyl residue) and anteiso (having a terminal iso-butyl residue) series of varying chain length, with practically all the acids being saturated.

With development of analytical techniques the number of aliphatic alcohols reported has increased from 17 in 1955 to 69 in 1974. The monoalcohols and diols consist of normal, iso and anteiso series. Further studies showed that cholesterol ( $C_{27}H_{45}OH$ ) and the triterpene alcohols are the major components of wool wax alcohols. They are present in equal amounts and together they represent about 72% of total unsaponifiable material. The total aliphatic alcohol represents about 22% of the wax composition (Collins and Davidson, 1997).

Wool wax is a yellowish wax-like substance which melts at 37–38°C and is soluble in many organic solvents. It retains its creamy consistency even when mixed with an approximately equal quantity of water. Lanoline, widely used in cosmetic preparation, is a mixture of purified wool wax with 20% water.

Dirt, water-soluble suint or dried perspiration and wool wax are removed by scouring wool with soap and alkali before dyeing and printing. After separation during scouring, wool wax gets contaminated with soap or detergent and suint and is, therefore called wool grease, as distinct from wool wax. Burrs or VMs such as thorns or seed coats, which sheep pick up during grazing, may also present. These impurities are removed by a strong sulphuric acid treatment called carbonisation.

### 3.3 Aims of preparatory processes

The aims of preparatory wet processing are as follows:

1. Uniform power of absorption for dyes and chemicals in subsequent processes.
2. An even water imbibition value.
3. Removal of all types of impurities including broken seeds, etc.
4. Minimum damage of the material.
5. Absence of creases and wrinkles.
6. High whiteness value.

Pre-treatment, however, is non-added-value stage of the colouration process and the pre-treatment stage is often not optimised. Frequently excess quantities of chemicals, auxiliaries and utilities (water, steam, electricity and time) are used in preparatory processes. This results in a high carry-over of preparation residues (cotton impurities and preparation auxiliaries) that will have negative influence on both dyeability and the dyeing system, or will require long multi-stage intermediate wash-off procedures.

The pre-treatment process must balance the requirements of the dyeing and finishing stages and the intended end-use of the textile material.

### 3.4 Preparation of cotton materials

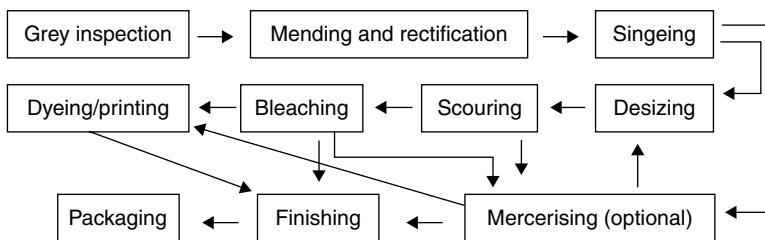
The water-intensive wet processing steps of cotton fibre, yarn and fabric generate large volumes of wastes, particularly from alkaline scouring and subsequent dyeing processes. These wastes include large amounts of salts, acids and alkali. In view of the 40 billion pounds of cotton products that are prepared annually on a global scale, it becomes clear that the preparation process is a major source of harsh chemicals released into the environment.

Cotton is mostly processed in fabric form and rarely in fibre form. Some quantities of cotton material are prepared and dyed in yarn form, mainly for sewing and embroidery threads and for coloured yarn in woven and knitted designs. The different stages for preparatory processing of cotton fabrics are shown in Fig. 3.1. There are a number of alternate sequences. For preparation in yarn form, obviously inspection and desizing steps do not arise.

### 3.5 Inspection and mending

Grey fabrics are first inspected for conformity with the standard. They are sorted into lots. Each lot should be of the same width and similar weight per unit length so that they can be processed together. All the pieces of the lot are sewn end to end with loops, which can be easily removed after finishing. The seams should be 10 mm wide and for certain processing, e.g. chain mercerising and continuous drying, the seams should be wider (15 mm) and stronger. In some textile units, gluing or bonding of fabric is used instead of sewing in order to reduce the amount of rags. A polymer coating is applied to the ends of the fabrics to be bonded, which are then placed between heated metal surfaces. The polymer melts and binds the ends of the pieces.

The fabric after sewing or bonding end to end is passed slowly over an inspection table with an inclined frosted glass top. The table is illuminated with a fluorescent lamp fitted below. The illuminated fabric is visually



3.1 Sequence of operations in cotton fabric processing.

inspected for various weaving faults, damage, etc., which are suitably marked with coloured pencils. The marked fabric is then repaired for missing end (warp) or pick (weft) by mending, or the damaged portion is cut off which may otherwise entangle with machine parts causing excessive damage.

Until recently, this important step was considered to be a routine one. However, with the enforcement of stringent quality control regulations, scientific practices or electronic devices have quickly overcome bad practices such as nominal checking or no checking. The use of electronic instruments has enabled precise inspection of a piece, leaving no scope for unnecessary cutting. Stains, holes, thick and thin places and warp/weft thread breaks can now be detected by laser beams as in the Sick-scan-system, Ko-Re-Tra of E. Sick, GmbH (Karmakar, 1999). The apparatus operates on three different principles – coaxial (emitter and receiver at the same place), remission (receiver at a freely adjustable angle) and transmission (receiver on the opposite side of the fabric). The light source is helium-neon laser or a xenon high-pressure lamp.

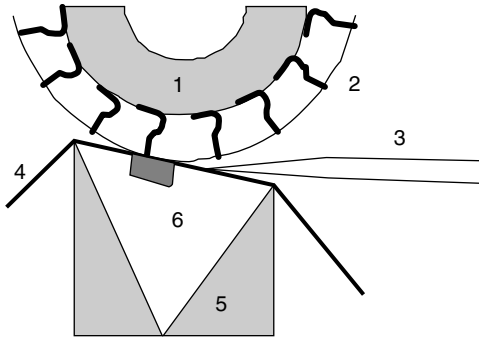
An unmended hole or an oily stain can give rise to either tearing or hole-formation in bleaching or to patchy dyeing. In case of irreparable physically damaged portions or heavily oil-stained portions, the portions are best cut off and the pieces are re-stitched. The most common accidental impurities are stains caused by various agents, which are easily visible in the embedded portions. Most of the stains are removed by local spotting with an efficient stain remover followed by thorough rinsing and soaping.

The stain removers are generally solvents (e.g. acetone, methylated spirit, petrol), solubilising agents (e.g. acetic or oxalic acid), oxidising agents (e.g. sodium hypochlorite solution, potassium permanganate and oxalic acid or hydrogen peroxide) or reducing agents (e.g. sodium hydrosulphite).

### **3.6 Shearing and cropping**

After inspection and mending, small projected yarns may remain on the surface of the fabric, which obstruct adsorption of dyes on the fabric surface during dyeing and printing processes. They may also be entangled with machine parts causing damage of the materials. These projected yarns are removed by a process called shearing and cropping, during which the projected fibres or yarns are cut from the fabric surface.

In shearing operation, dry or occasionally slightly dampened fabric is drawn between a shearing table and the shearing device, which consists of a shearing cylinder and a ledger blade. The action is similar to that of a lawn mower. The shearing machine may have two or four cutting heads. The various components of a shearing machine (Rouette, 2001) are shown in Fig. 3.2 and are discussed below.



3.2 Shearing machine with hollow table (see discussion in text for explanation of components).

The shearing cylinder (1) is a thick-walled hollow cylinder with a bearing journal firmly inserted at both ends. The speed of the cylinder during shearing is between 500 and 2000 rpm depending on the fabric to be sheared. Depending on the particular design, the cylinder has 10–24 or, in the case of a carpet shearing machine 40 spiral blades (2) mounted securely around its circumference. In a conventional shearing cylinder the shearing spirals are fitted onto the cylinder at equal distances regardless of the number of spirals used. In modern shearing machines as in Multicut MC-5, the spirals are arranged asymmetrically to avoid periodic variation of pile length.

The ledger blade (3) is a 10–12 cm wide knife blade, 3–6 mm thick, corresponding in length to the width of the shearing machine. This is ground on its underside for approximately 3 cm towards the cutting edge. An absolutely uniform contact surface between the cutting edge of the ledger blade and the fabric is ensured. The opposite side of the blade is screwed or clamped to the support beam. The cutting angle of the blade should be small in order to obtain the cleanest possible shear.

During shearing the fabric (4) is passed over a shearing table (5) which may be hollow or pointed. Seams must not be allowed to pass under the shearing device; otherwise they will be cut open. Seam-joint sensors (6) lift the shearing rolls away from the fabric surface or the shearing bed is lowered, whenever a seam-joint reaches the shearing point. Rotating brushes are installed both in front of, as well as behind, the shearing device to align the fibres correctly for shearing and to remove cut ends after shearing, respectively.

Shearing has assumed great importance recently in view of its potential for improving fabric quality. In the case of polyester blended fabrics, in particular, shearing has proved to be of great value in reducing the incidence of micro beads for dyed fabrics. In the case of cotton fabrics, in particular, care should be taken to see that the shearing blades do not scratch the surface of the fabric, which otherwise may cause dyeing defects during subsequent dyeing.

### 3.7 Singeing

When yarn is made from short-staple fibres, the two ends of the fibre may not be embedded inside the yarn and are projected due to the twist imparted during spinning. For multi-filament yarns, some filaments may break or cut in places and are projected from the surface. Singeing or gassing is a very effective method for removal of these projected fibres. Though singeing is not essential for all types of fabrics. However, it is important for several reasons namely:

- (a) The surface of yarn or fabric appears fuzzy or hairy due to the presence of projected fibres or yarns and gets soiled easily. The smooth lustrous appearance of yarn (e.g. sewing and embroidery threads) and fabric is achieved by singeing.
- (b) The protruding fibres obstruct subsequent dyeing and printing processes in an uncertain manner. Singeing is almost essential with goods intended for printing.
- (c) The goods to be mercerised are singed to develop maximum lustre in the fabric.
- (d) For polyester/cellulosic blended fabrics, singeing is the best method for controlling pilling. Sometimes double singeing is done to minimise pilling.

The object of singeing is to burn off projecting hairs without scorching or otherwise damaging the body of the fabric. Improper singeing may cause irreparable faults. Singeing of fabric vegetable fibres is done in grey state as singeing causes slight yellowing which is rectified by subsequent bleaching. On the other hand, synthetic fibres and their blends are to be singed after dyeing, otherwise molten amorphous beads take up more dyes making dark spots. Polyester melts at higher temperature and requires a powerful flame.

The types of singeing machines commonly employed are as follows:

1. Plate singeing machine
2. Rotary cylinder or roller singeing machine
3. Gas singeing machine.

The first two methods are based on passing the fabric over internally heated (750°C) red-hot metallic parts of curved copper plates (2.5–5.0 cm thick) in plate singeing and of a rotating copper cylinder in roller singeing at a very high speed. Special traversing arrangements for the fabric are provided to prevent local cooling and wear and tear of the metallic parts. Plate and roller singeing are obsolete nowadays, because of insufficient singeing and a typical hardness on the fabric produced by them. Gas-fired singeing machines have achieved universal approval. However, contact singeing or roller singeing is still used to singe velvet fabrics.



In a gas singeing machine, the fabric in open width is first passed (with the help of a guide roller) through a pair of hot metallic drying cylinders for drying as well as for warming up. The fabric is then passed through a number of weft straighteners or curved rollers to remove weftwise creases from the fabric. The fabric is then subjected to cleaning by means of brushes, which rotate in a direction opposite to the fabric motion. The brushes are placed inside a chamber and an exhaust fan removes the fluff and dust collected by the brushes. Then the fabric passes over gas burners with ceramic nozzles where singeing is carried out. Two or more gas burners are used and the passage of the fabric is so arranged with the help of a large number of guide rollers so that both sides of the fabric can be singed in a single passage. The same set or two different sets of burners may be used for singeing both sides of the fabric by threading the fabric suitably. It is also possible to adjust the flame height and consequently the heat intensity, by altering the pressure of the gas or air–gas mixture, and is expressed in terms of the height of the manometer in centimetres.

After singeing, the fabric is still hot and may carry some sparks along with it. It is, therefore, drawn by the roller of a mangle through a trough of water called a quench box, in which all sparks are extinguished. To avoid wetting of the fabric, quenching by passage through steam is also possible. An additional desizing compartment may be incorporated so that the materials may be impregnated with the desizing solution followed by squeezing.

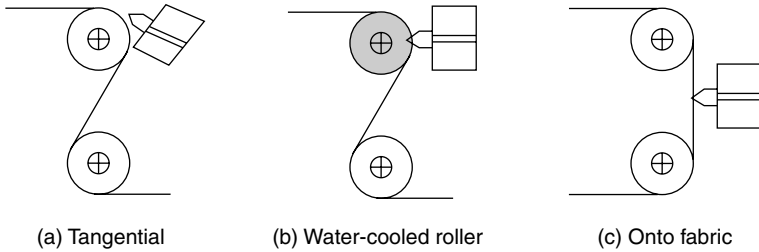
Two main methods of singeing are direct flame singeing and indirect flame singeing. The important direct flame singeing parameters are as follows:

- Singeing position
- Flame intensity
- Fabric speed
- Distance between the fabric and the burner
- Moisture in the fabric.

If any one or more of the above parameters are not optimal, the result may be faulty singeing. There may be singeing faults which are optically demonstrable and are quite easily remedied during the actual working process. On the other hand there may be some singeing faults which are not visible until dyeing and which, once occurred, can no longer be repaired.

The common faults in singeing are as follows:

- Incomplete singeing
- Uneven singeing (widthways)
- Uneven singeing (lengthways)
- Thermal damage or reduction in tear strength.



3.3 Burner positions in a modern gas singeing machine.

Depending on the type of fabric, singeing positions may require to be varied (Fig. 3.3) such as (Bhagawat, 1991):

- (a) Tangential singeing
- (b) Singeing on water-cooled rollers or with counteracting cool air
- (c) Singeing onto free-moving fabric.

### 3.7.1 Tangential singeing

The flame impinges on the fabric at an angle. Consequently, only protruding fibres are burnt and the fabric surface is not directly affected. This is ideally suited for lightweight and sensitive fabrics. It is also suitable for synthetic filament fabrics which require mild singeing just to remove tiny broken filament-ends only.

### 3.7.2 Water-cooled roller singeing

The flame impinges directly on the fabric and it is reflected back to the surface by the water-cooled roller situated at the back of the fabric. An elastic steam-air cushion, formed inside the fabric, resists deeper penetration of the flame and singeing occurs only at the surface. The fabric also remains cooler and heat-sensitive fabrics are protected from the singeing heat. It is most suitable for synthetic, blended and open-structured fabrics.

### 3.7.3 Singeing onto fabric

The flame passes through the fabric and both sides of it are accessible to the flame. The flame enters the interstices of the fabric and, therefore, imparts good singeing. This method is very suitable for fabrics made from natural and man-made cellulosic fibres, and for heavy industrial and technical fabrics.

**Table 3.4** Gas singeing parameters for various types of fabrics

Fabric variety	Fabric weight (g/m <sup>2</sup> )	Burner position (Fig. 3.3)	Fabric distance from flame (mm)	Flame intensity (water column, mm)	Machine speed (m/min)
Pure cotton	80–140	(c)	8	150	90–110
Cotton/viscose	160–220	(c)	7	120–130	80–90
Cotton/polyester	70–100	(b)	7	120–130	100
Polyester/viscose	Above 250	(c)	6	160	80–90
Lightweight, cotton or blend	50–120	(a)	–	80	100
Woollen	–	(b)	10	70	45–70
Corduroy or ribbed, cotton or blends	–	(b)	8–10	150	100
Velvet and velour	Contact (roller singeing) singeing at a temperature of about 700–800°C.				

For proper singeing, the burner is kept very near to the fabric in tangential singeing, while the flame should meet the fabric at right angle position in the other two cases.

The recommended conditions for singeing of a few typical varieties of fabrics (Bhagawat, 1991) are given in Table 3.4.

### 3.8 Enzymatic processing

In the textile industry the use of amylase enzymes for starch splitting began around 1857 when malt was used to remove gum from fabrics before printing. The enzymes are now largely used for various pre-treatment processes of textile materials, namely desizing, scouring and bleaching of cellulosic materials, degumming of silk, carbonising, bleaching and shrink-resist treatments of wool.

Enzymes are biological catalysts. They are naturally occurring proteins capable of catalysing specific chemical reactions, and, being catalysts, facilitate the reaction without being consumed. The advantages of enzymatic processing are (Paulo and Gübitz, 2003):

1. Enzyme-catalysed reactions are several orders of magnitude faster than chemically catalysed reactions.
2. Enzymes are highly specific in chemical reactions and they rarely form by-products.
3. Enzymes catalyse reactions under comparatively milder conditions of temperature (below 100°C), pressure (atmospheric) and pH (around neutral).

4. Consequently, enzymatic treatments offer savings in chemicals and energy and have less or no impact on the environment. The enzymes are fully biodegradable.

Most enzymes are much larger than the substrates they act on, and only a small portion of the enzyme (around 3–4 amino acids) is directly involved in catalysis. The region that contains these catalytic residues, binds the substrate, and then carries out the reaction is known as the active site. Enzymes can also contain sites that bind cofactors (non-protein activators), which are needed for catalysis.

It has been suggested that the enzymes show specific catalytic action because both the enzyme and the substrate possess specific complementary geometric shapes that fit exactly into one another. This is often referred to as the ‘lock and key’ model (Nolan, 1998). However, while this model explains enzyme specificity, it fails to explain the stabilisation of the transition state that enzymes achieve.

The ‘lock and key’ model has proven inaccurate, and the induced fit model suggested by Daniel Koshland (1958) is the most currently accepted enzyme-substrate-coenzyme model. Since enzymes have rather flexible structures, the active site is continually reshaped by interactions with the substrate. As a result, the substrate does not simply bind to a rigid active site; the amino acid side chains which make up the active site are moulded into the precise positions that enable the enzyme to perform its catalytic function. In some cases, such as glycosidase, the substrate molecule also changes shape slightly as it enters the active site. The active site continues to change until the substrate is completely bound, at which point the final shape and charge are determined.

Deactivation of enzymes may occur by competitive or non-competitive chemicals called ‘bogies’ in the processing bath. All enzymatic systems function best within a narrow range of pH and temperature – too far outside the range, the enzyme becomes deactivated by changes in three-dimensional structure. As the enzyme twists and coils into a shape that prevents sorption between enzyme and substrate, catalysis no longer occurs.

Most enzymes are inactivated or destroyed at temperatures over 75°C. Once destroyed, they cannot be revived or reactivated. Currently thermo-stable enzymes (*α*-*Bacillus subtilis*, *α*-*Bacillus licheniformis*, etc.) are available which can withstand temperatures up to 90°C. Certain enzymes require some specific bivalent metallic ions (e.g. Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, etc.) as activators which most likely act by stabilising the enzyme–substrate complex or sensitising the substrate to the attack of enzymes. Certain chemicals such as alkalis, antiseptics and acid-liberating agents tend to inhibit the enzyme activity.

Enzymes are principally classified and are named according to the chemical reaction they catalyse. In other words, they are named by the substrate on which

they act. An enzyme name is assigned to a group of proteins with the same catalytic property, even if they are obtained from different sources. Some common types of enzymes and their specific activities are as follow (Shenai, 1984):

- Lipases: Split fats into glycerol and fatty acids.
- Amylases: Split starch (amylase) into dextrin and sugars.
- Proteases: Split proteins into soluble polypeptides and amino acids.
- Pectinolytic or pectinases: Degrade pectin.
- Zymases: Convert glucose into alcohol and carbon dioxide.
- Cellulases: Degrade cellulose to soluble products.
- Catalases: Convert hydrogen peroxide into water and oxygen.
- Saccharidases: Convert polysaccharides to glucose.

The application of enzymes in various stages of textile processing may be summarised as follows (Holmes, 1998):

- Desizing: Amylase, lipase.
- Scouring: Pectinase, cellulase.
- Bleaching: Oxidoreductase, xylanase.
- Dyeing: Oxidoreductase.
- Finishing: Cellulase, oxidoreductase, lipase.
- Composting (biodegradation of textile wastes): Cellulase, protease, nylonase, polyesterase.

Using bioengineering principles, new sources of enzymes are being discovered, isolated and cultured for commercial use. Major companies involved in the preparation and marketing of enzymes useful for textile industry are Novoenzymes (formerly Novo Nordisk), Dystar, Clariant, Genencor, etc.

Non-ionic surfactants are essential for effective enzymatic treatments. They are compatible with enzymes, while anionic/cationic surfactants may form complex with enzymes. The presence of non-ionic surfactants in the enzymatic solutions favours enzymes' biological functions. Mechanical agitation can increase apparent enzyme activity and efficiency in scouring. However, enzymes may be denatured by mechanical agitation with high shear forces (Li and Hardin, 1997b).

Implementing an enzyme safety programme is important for limiting exposure to enzymes and maintaining employee health and safety in the workplace. According to an American Soap and Detergent Association (SDA) document, exposure to enzymes may cause irritation and/or respiratory allergies. Skin and eye contact with proteolytic enzymes may cause irritation. Other classes of enzymes are less irritating or pose no risk of irritation. However, formulation ingredients may be irritants. Exposed areas

should be protected by using hand and eye protection and other protective wear (ETA, 2000).

### 3.9 Desizing process

'Size' is imparted to the warp yarn before weaving to prevent breakage or damage of warp yarns during weaving due to abrasion. The presence of size on the fabric makes it stiff and renders its treatment with different liquors used in dyeing and finishing difficult. Therefore, one of the initial steps in wet processing is the elimination of size and water-soluble admixtures, the operation being called desizing.

The typical sizing materials are as follows:

- (a) Natural starches from potatoes, maize, rice or tapioca.
- (b) Chemically modified starches (ethers or esters).
- (c) Organic polymers, e.g. polyacrylates, carboxymethylcellulose, methylcellulose, polyesters or polyvinylalcohol (PVA).
- (d) Solvent-soluble materials, e.g. copolymers of methyl methacrylate.

About 75% of the sizing agents used throughout the world consists of starch and its derivatives because of its low cost and high effectiveness as a sizing material on cellulosic textiles. Starch is difficult to remove, as it is not soluble in water or in normal scouring liquor. Removal of starch before scouring minimises the work required in subsequent cleaning processes – reduced concentrations of chemicals are required in subsequent scouring and bleaching processes. Moreover, alkali-degraded products of starch are of reducing nature and may reduce dyes if dyed materials are scoured.

While drying after sizing at high temperature, the sizing materials are baked to a cake, which is often extremely difficult to remove from the yarn. Occasionally, emulsifying agents are added in the size to facilitate their removal. The term desizing is restricted to the removal of starch, while wax and tallow are loosened during desizing and are removed during subsequent scouring process.

Chemically starch is a poly- $\alpha$ -glucopyranose in which straight chain amylose and branched chain amylopectin polymers are present. Both the constituents are insoluble in water, but can be solubilised by hydrolysis. Under favourable conditions, starch can be progressively hydrolysed to the following products with varying solubility in water:

Starch (insoluble)  $\rightarrow$  Dextrin (insoluble)  $\rightarrow$  Dextrin (soluble)  $\rightarrow$  Maltose (soluble)  $\rightarrow$   $\alpha$ -glucose (soluble).

In desizing, the hydrolysis reaction is carried out up to the stage of soluble dextrin only and not up to the stage of  $\alpha$ -glucose to avoid degradation of cellulose.

Solubility of starch may be promoted by the action of acids, oxidisers, alkalis and enzymes. If proper care is not taken, acids and oxidisers not only attack starches but also cellulose itself. Hydrocellulose and oxycellulose are formed as degradation products and the fabric becomes weaker. The desizing process is, therefore, carried out with lower concentration of desizing agents at lower temperature. The destruction of cellulose is minimised, but the time required to complete desizing is appreciably high.

Preparatory processes create 60–70% of the total Chemical Oxygen Demand (COD) load of the process-house effluent, of which desizing amounts to roughly 80%. This means that 50–55% of the total COD load originates from desizing. About 75% of the sizes used are starch-based and with the exception of Carboxymethylcellulose (CMC) sizes, are not suitable for recycling.

The purpose of desizing is not a complete elimination of all the sizes on the fabric. Rather, the desizing process must be carried out in such a way that subsequent processes can be carried out in the best possible manner and without difficulty.

The classical low-cost desizing process for starch sizes is pad-batch desizing. Impregnation and padding is done in the trough attached to the singeing machine followed by long time batching. The difficulties are insufficient liquor pick-up if the bath is too small, size accumulation in the impregnation bath, messy batching station (especially with PVA), fabric transfer problem after batching, stickiness of the fabric, high rinsing water requirement (8–10 L/kg), high effluent volume of low concentration (1.2–1.5%), longer processing time and logistics problems.

Water-soluble synthetic sizes may be removed on full-width washing machines, preferably with roller vats. The advantage of this method is that it can be carried out in common washing machines. The disadvantages are the time needed for swelling, long washing zone, high rinsing water requirement (8–10 L/kg) and high effluent volume of low concentration (1.2–1.5%).

In a modern impregnator such as the BEN-INJECTA (Benninger, Germany), the fabric is guided through two narrow castings where steam and water meet both sides of the fabric, separately or in a desired mixture. Due to the design of the steam injector slots and the geometry of the shafts, steam ejects at a very high velocity on the fabric and thus contains high kinetic energy. Shock heating of the fabric at the entry of the first casting, combined with strong kinetic energy from the steam–water mixture, means high molecular weight products, such as size, can be separated without swelling by lowering of viscosity due to high kinetics (i.e. due to thixotropic behaviour of size) with no gumming of the fabric and machine parts. The washing process is completed in a subsequent short washing zone. Only counter-flow water from the following compartment at a liquor circulation of 300 L/min is used, i.e. no additional fresh water in the first bath. The

consumption of water/liquor in the process is low – around 1–3 L/kg with consumption of 0.4–0.6 kg saturated steam. This results in a highly concentrated effluent flow – ideal for recycling of synthetic sizes. The sizes soluble or insoluble in water can be removed to the extent of 85–95%. Starch sizes may be pre-wetted with a small amount of enzymes for partial depolymerisation (Weber and Ströhle, 1997).

Starch desizing methods can be classified as follows:

1. Hydrolytic methods
  - (a) Rot steeping
  - (b) Acid steeping
  - (c) Enzyme steeping.
2. Oxidative methods
  - (a) Chlorine desizing
  - (b) Chlorite desizing
  - (c) Bromite desizing
  - (d) Peroxy compounds.

Chlorine gas, sodium chlorite and sodium bromite are not eco-friendly and are no longer used for desizing.

Hydrolytic methods consist of degradation of starch into different intermediate compounds and finally into its monomer glucose. Hydrolysis is mostly carried out by enzymes, either those inherently present in water (rot steep) or added externally (enzyme steep) or partly by mineral acids (acid steep). Generally hydrolysis processes are slow and require significant time; hence those are mostly batch processes. However, they are comparatively safer than oxidation processes.

Oxidising agents attack the glucose ring or the ether linkage forming carboxyl or aldehyde groups. Both reactions ultimately result in depolymerisation of starch into water-soluble products. However, cellulose being of similar structure to that of starch is not spared and some degradation of cellulose into oxycellulose is inevitable. The oxidative desizing processes are, therefore, to be carried out carefully to minimise such degradation. Oxidising agents used for desizing also have bleaching actions on cellulose. Hence, partial bleaching occurs during desizing.

### 3.9.1 Rot steeping

In this oldest and cheapest hydrolytic method, the fabric is first passed through a padding mangle, in which warm water at 40°C is kept and the fabric is squeezed to about 100% expression. The fabric is then allowed to stand for about 24 h at 35–40°C or overnight at 60°C in open space or in an open box. The micro-organisms, naturally present in water, multiply



and secrete starch liquefying (hydrolysing) enzymes, which solubilise the starch. The fabric is finally washed with water, when most of the starch and water-soluble matters present in the fabric are removed. However, it is a slow process and it requires an enormous floor space for storing the water-impregnated fabric. There is always a chance of mildew formation during storage of the fabric.

### 3.9.2 Acid steeping

The fabric is impregnated with 2.5 g/L sulphuric or hydrochloric acid solution at room temperature (30°C) followed by storage for about 6–8 h. Faster desizing (within 1–2 h) is possible using stronger solution of acid (e.g. 10 g/L). The process called ‘souring’ is almost indispensable for low-quality cotton fabric. Hydrolysis of starch by mineral acid is an exothermic process and the temperature may even rise up to 50°C. During storage the fabric should not be allowed to dry, otherwise the concentration of the acid in the fabric will increase with subsequent damage of the fabric. By the acid steeping method, almost all the starch present in the fabric may be liquefied. A subsequent wash removes the solubilised starch. The acid-treated fabric should never be allowed to dry before wash, otherwise mineral acid at high temperature reacts with cellulose forming hydrocellulose.

The loss in weight after acid desizing is always more than that after rot steeping, because the former process dissolves nearly all the mineral impurities. The main disadvantage of acid steeping is that there is always a chance of tendering of the fabric by acid hydrolysis unless proper care is taken.

### 3.9.3 Enzyme steeping

Desizing by enzymes is the safest method. In general, enzymatic desizing agents may be divided into two main types:

1. dextrinogenic or  $\alpha$ -amylases
2. saccharogenic or  $\alpha$ -amylases.

Both hydrolyse glucosidic linkages in the starch molecules, but the points, at which the reaction occurs, are different. The  $\alpha$ -amylase attacks the chain at random so that the DP of the starch (both number and weight averages) is rapidly reduced. Water-soluble dextrans form with consequent rapid decrease in the viscosity of starch pastes.

The  $\alpha$  amylases successively remove terminal maltose units, so that the polymer chain is shortened gradually. The presence of maltose units significantly decreases the number average DP, leaving the weight average

DP unchanged. With the amylopectin fraction, the action of  $\alpha$ -amylase is arrested at the branch points, so that a considerable quantity of the original polymer remains.

Starch-degrading enzymes, which may also be classified according to their source of occurrence, are as follows:

1. Enzymes from animal sources such as slaughterhouse waste – clotted blood, pancreas, liver, etc.
2. Enzymes from vegetable sources
  - (a) Malt extract
  - (b) Bacterial.

Pancreatic enzymes are prepared from slaughterhouse waste. The waste materials are first extracted with water and concentrated under vacuum, followed by precipitation by adding alcohol in which the enzymes are insoluble. The enzymes are filtered and finally dried. Malt enzymes are made from germinated barley, while bacterial enzymes are produced by growing culture of certain micro-organisms on suitable media (e.g. wort-beer prior to fermentation) under controlled conditions for about a week.

The optimum conditions for enzyme desizing are shown in Table 3.5 (Shore, 1995).

Time required for desizing depends on the method of application, kind of fabric (tightness of weaving, weight, etc.) and the temperature and concentration of the enzyme. The incubation times in various methods are reported (Paulo and Gübitz, 2003) to be as follows:

Jigger:	2–4 ends (60–100°C)
Winch:	30 min (90–100°C)
Cold pad-batch:	6–24 h (15–40°C)
Hot pad-batch:	3–8 h (60–70°C)
Pad-steam:	15–120 s (90–110°C)

Table 3.5 Optimum conditions for enzyme desizing

Diastase/Amylase	pH	Temp. (°C)	Time (h)	Effects 1 and 2
Malt	4.5–5.5	55–65	12–24	– +
Pancreatic	6.5–7.5	40–55	12–24	++
Bacterial	6.5–7.5	65–75	1–4	++
Bacterial (thermostable)	7.0–8.0	100–120	1–2 min	++

1. Sodium chloride, 2. Calcium ion, – no effect, + enhancement.

Source: Adapted from Shore (1995).

The amounts used depend on the activity of the product. The recommendations for Aquazyme 120 L from Novo Nordisk (120 refers to the strength of the enzyme) for various machines are as follows:

Quench box:	10–25 g/L
Winch:	2–10 g/L
Jigger:	2–10 g/L
J-box:	20–50 g/L
Combi-steamer:	20–50 g/L

Calcium ions stabilise the enzymes. Hence, chelating agents which inactivate calcium should not be used during enzyme desizing. Wetting agents and non-ionic surfactants can be used to enhance enzyme penetration and adsorption, fibre swelling and to promote the removal of waxes, soils and synthetic sizing agents. Anionic and cationic surfactants may inactivate enzymes. Lubricants are recommended in jet and rotary washers, to reduce formation of crease marks and streaks. After enzymatic treatment, the fabrics should be washed off above 80°C in alkaline liquor followed by a wash in neutral liquor.

It is often the practice to include some beef tallow or other fat in the size bath in order to improve the lubricity of the sized yarn after drying. Much time is required to remove them during scouring. It is, therefore, proposed that lipase enzymes be included in the amylase desizing bath to catalyse hydrolysis of the fat, the hydrolysis products being glycerol and fatty acid. An efficient synergistic removal of starch is possible when lipase is present in addition to amylase.

#### 3.9.4 Peroxy compounds

The possibility of using sodium persulphate or hydrogen peroxide has been suggested but their commercial use to date is small.

Three peroxodisulphates,  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (commonly known as persulphates), are available as sodium, potassium and ammonium salt. All salts are equally effective, but sodium salt is preferred. Potassium salt has poor solubility; ammonium salt liberates ammonia from alkaline desizing liquor.

##### *Continuous method*

0.3–0.5% persulphate and 1–5% caustic soda fed to saturator separately maintained at temperature less than 43°C. After impregnation the material is steamed at 90°C for 5 min. The desizing time is only 30–60 s at 110–130°C, but there is little advantage of temperature exceeding 110°C.

*Cold pad-batch method*

The fabric is padded with 0.5% persulphate, 0.5% tetrasodium pyrophosphate and 0.5–3.0% caustic soda. The padded fabric is batched for 4–8 h before wash-off. All percentages are % o.w.m. (on the weight of material).

The persulphates are not recommended for kier or other circulating equipment with slow heating rate. The degree of starch degradation achieved in persulphate desizing is less than that obtained with enzymes, but for many purposes it is adequate and subsequent peroxide bleaching will usually complete the removal of size.

PVA is water-soluble, but redissolving of PVA size is hampered by heat and gelling by caustic alkali. Alkaline conditions may produce chromophores and pungent odour on PVA sized fabric in the presence of oxidising agents. Desizing of such sizes with hydrogen peroxide is, therefore, to be carried out under mild alkaline conditions.

*Pad-steam desizing method*

The fabric is padded with 0.2–0.4% o.w.m. hydrogen peroxide at pH 6–8 followed by steaming at 90–100°C for 15 min.

*Two-bath process*

The fabric is treated with a 0.8% solution of hydrogen peroxide at 90°C at neutral pH. Without intermediate rinsing, the fabric passes into a second bath containing 0.5% caustic soda before final rinsing at 70°C (minimum).

Alternatively, the fabric may be treated with 1–2 volume hydrogen peroxide along with 7–15 g/L caustic soda followed by short steaming (3 min).

The use of special grade hydrogen peroxide with magnesium sulphate as stabiliser allows preparation of desizing pad liquors of adequate stability at 60°C with pH 12 or above. The stabiliser does not impair desizing when the fabrics are subsequently steamed at 90°C. No magnesium sequestering agent should be used.

Recommended conditions for oxidative desizing reported elsewhere (Shore, 1995) are shown in Table 3.6.

The demerits of oxidative desizing are (Dickinson, 1987) as follows:

1. Similar to other desizing processes, size recovery is not possible by this method. However, after size recovery, residual size may be quickly and efficiently removed by oxidative treatments.
2. Another obstacle, but not limitation, is the need for good control of the desizing system and good equipment for application. Enzymes show greater tolerances to concentration variations.

*Table 3.6* Recommended conditions for peroxy desizing

Quantities in % o.w.m.	Recipe 1	Recipe 2	Recipe 3
Magnesium sulphate	0.005	0.005	0.005
Caustic soda, solid	2–6	2–4	9–12
Stabiliser	0–1	0–1	0–1
DTPA (diethyltri-amine pentaacetic acid, 40% solution)	0.2	0.2	0.2
Hydrogen peroxide (35%)	5–15	5–15	5–15
Or Sodium persulphate	0.2–0.5	0.2–0.5	0.2–0.5
Wetting agent	0.2–0.5	0.2–0.5	0.2–0.5
Temp. (°C)	100	100	120–130
Time (min)	<15	15–60	1–2

3. Adverse effects of metal contamination. Many quench boxes of singeing machines contain brass components, which are damaged by oxidants.

Based on availability, cost and effectiveness, only two chemicals are of prime importance for oxidative desizing – peroxydisulphates and hydrogen peroxide.

Fabrics made from typical regenerated cellulosic fibres are desized by the same processes as for cotton. Care should be exercised with oxidative desizing in terms of both alkali and oxidant concentrations, which should be no more than half of those used for cotton. Most warps contain starch-based sizes and so enzyme desizing is customary. In case of carboxymethylcellulose size, a cold swelling process followed by hot washing with a detergent is adequate (Hickman, 1995).

Viscose and most other regenerated cellulosic fibres dissolve in caustic soda liquor at about 6.5% by mass (70 g/L), so causticisation rather than mercerisation is carried out using 3.3–5.5% NaOH by mass (35–60 g/L) to enhance wetting or dyeability. Polynosic fibres or high wet modulus (HWM) fibres are more resistant to alkali than regular viscose.

The objectionable effects of viscose manufacturing plants on the environment have been universally recognised for a long time, but it was not until the 1970s that the use of an alternative solvent for wood pulp emerged as a serious possibility.

For the development of regenerated fibre, eco-friendly N-methylmorpholine-N-oxide (NMMO) was found to be the most suitable solvent and eventually in 1988 Courtaulds established full-scale manufacture of Tencel, the first lyocell fibre (Taylor and Mears, 1991). The tenacity (wet and dry) of lyocell fibres is markedly higher than that of cotton or any other type of regenerated cellulosic fibre. Tencel A100 (Acordis) and Newcell (Akzo Nobel) are non-fibrillating modified lyocell fibres. Scouring with sodium

carbonate at concentrations up to 20 g/L causes no loss of non-fibrillation performance. Pad-batch bleaching with 25 g/L hydrogen peroxide and 4 g/L sodium hydroxide is recommended for pastel shades and fluorescent whites.

### 3.10 Scouring of cotton and other cellulosic fibres

Scouring is the most important wet process applied to textile materials before dyeing or printing. It is mostly a cleaning process in which foreign matter or impurities are removed. The scouring process, while purifying the  $\alpha$ -cellulose, imparts the hydrophilic character and permeability necessary for the subsequent processes (bleaching, mercerising, dyeing or printing). Good scouring is the foundation of successful finishing. The performance of a scouring process is judged by the improvement in wettability of the scoured material.

More specifically, scouring is conducted in order to remove unwanted oils, fats, waxes, soluble impurities and any particulate or solid dirt adhering to the fibres, which would otherwise hamper dyeing, printing and finishing processes. The process essentially consists of treatment with soap or detergent with or without addition of alkali. Depending on the fibre type, alkali may be weak (e.g. soda ash) or strong (caustic soda).

When soap is used, a good supply of soft water is necessary. The metal ion ( $\text{Fe}^{3+}$  and  $\text{Ca}^{2+}$ ) present in hard water and pectin of cotton can form insoluble soap. The problem is more acute when scouring is carried out in a continuous process involving a padding bath where the liquor ratio is much lower than in the batch process; the chelating or sequestering agent, e.g., Ethylenediaminetetracetic acid (EDTA), Nitrilotriacetic acid (NTA), etc., may be used to prevent scum and film formation. A high-quality synthetic detergent provides a good balance with wetting, cleaning, emulsifying, dispersing and foaming properties, thus providing good cleaning ability. Anionic, non-ionic detergents or their blends, solvent-assisted detergent blends and soaps are mostly used for scouring. For accelerating the scouring process, wetting agents in conjunction with high boiling solvents (cyclohexanol, methylcyclohexanol, etc.) are sometimes used, but the process may not be eco-friendly. The function of solvents is mostly to dissolve insoluble fats and waxes.

Builders are added to the kier-boiling bath to increase the activity of soap or detergents. These are generally salts such as borates, silicates, phosphates, sodium chloride or sodium sulphate. Sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) can additionally act as a detergent and buffer. The function of the buffer is to drive soap from the water phase to the fabric/water interface and consequently increase the concentration of soap on the fabric.

During boiling of cotton with caustic soda, entrapped air may cause oxidation of cellulose. This may be prevented by the addition of a mild reducing

agent such as sodium bisulphite or even hydrosulphite in the scouring liquor.

Scouring processes for different textile materials vary widely. Among natural fibres, raw cotton is available in the most pure form. The total amount of impurities to be removed is less than 10% of the total weight. Nevertheless, prolonged boiling is necessary as cotton contains waxes of high molecular weight, which are difficult to remove. The proteins also lie in the central cavity of the fibre (lumen) which is relatively inaccessible for the chemical used in scouring. Fortunately cellulose is unaffected by prolonged treatment with caustic solution up to the concentration of 2% in the absence of air. Hence, it is possible to convert all the impurities during scouring, except natural colouring matters, into soluble form, which can be washed away with water.

Scouring of cellulosic fibres other than cotton is quite simple. Bast fibres like jute and flax cannot be severally scoured owing to the chances of removal of several non-fibrous components with consequent damage of the material. These are generally scoured using soap or detergent along with soda ash. Jute is frequently used without further purification, but flax and ramie are usually scoured and often bleached. Jute for dyeing is pre-scoured but considerable amounts of lignin remain, leading to poor light-fastness.

Regenerated cellulosic fibres like viscose are more sensitive to alkali. As the man-made fibres are much cleaner, scouring with non-ionic or anionic detergents is sufficient.

Since natural impurities such as cotton wax, pectic substances and protein are associated mainly within the primary wall, the scouring process aims to remove this wall. The changes in the cotton materials caused by the treatment with boiling alkali are as follows (Trotman, 1968):

1. Hemicelluloses as well as cellulose fractions with a low DP are dissolved.
2. Saponifiable oils and fats are converted into soap.
3. Unsaponifiable oils and waxes are melted and emulsified by the soap.
4. Pectins and pectoses are converted into soluble salts of pectic acid and metapectic acid.
5. Proteins are hydrolysed with the formation of soluble sodium salts of amino acids or ammonia.
6. Water-soluble mineral substances are dissolved.
7. Insoluble dirt is removed and retained in suspension.
8. Sizing and other added impurities, if present, are broken into soluble products.

The required severity of the scouring and bleaching processes will depend on many factors, e.g. the type, colour and cleanliness of the cotton material,

the twist and count of the yarn, the construction of the fabric, etc. The aim of the bleacher is to remove the non-cellulosic impurities to a sufficient extent without modification of the cellulose. The impurities that are most difficult to remove are wax, seed fragments and oil stains.

In scouring, wax removal is not the only factor to be considered. The main barrier to the penetration of water is the primary wall of cotton. Study with an electron microscope shows that scouring causes numerous pits in the primary wall. The primary wall is modified when boiled with 1.5% caustic soda and is destroyed completely when boiled with 3% caustic soda at 40 psi pressure.

Scouring may be carried out on loose fibres, slivers, yarn or fabric but for ease of handling, fabric form is preferred. Surgical cotton is scoured and bleached in fibre form, whereas the yarns to be dyed are scoured in hank or in package (cones or cheeses) form. Cotton piece goods of light or medium weight are mostly scoured in rope form as it is cheaper to operate, while heavy-weight fabrics are best scoured in open width. Vigorous scouring is desirable for cotton goods, since they contain mechanically held particles of cotton seeds, husks and leaves, which may have escaped the ginning process, and which are supposed to be removed during scouring. Failure to remove them is detrimental, since their presence forms dark coloured spots on the fabric and they are dyed differently from those of the bulk material.

Scouring may be carried out in two forms:

1. Batchwise in kier, jigger, winch, overflow machines, etc.
2. Continuously in J-box, high-pressure reaction chambers, conveyor and roller steamers, etc.

High-capacity (500 kg to 5 tons) kiers are very popular for scouring mainly because of low cost of the machine, low processing and maintenance costs. Kiers are cylindrical type vessels of robust construction with a semi-circular bottom. The materials are uniformly loaded on a perforated false bottom through the manhole of the semi-circular top cover of the machine. An addition tank, a pump and a heat exchanger are fitted externally to the vessel. The vessel is first loaded with scouring liquor from the bottom to evacuate air trapped inside the textile material. Then the circulation is made clockwise – liquor falls through the sprayer at the top, percolates through the material, collects at the bottom and is sent through a heat exchanger. At the end of the boil, a scum may accumulate on the top layers of the fabric, which may be blown off by overflowing a small volume of liquor through a pipe from the top of the kier into the drain. Caustic alkalinity at the time of draining should not be less than 10% of the starting concentration in order to maintain the impurities in the suspended form.



The strength of caustic soda solution is generally varied according to the type of fabric. It is observed that high quantities of caustic soda are mainly used to remove 'kities' (broken cotton seeds) in the alkaline boiling off process. Only a little caustic soda is needed to remove the natural impurities. American practice (Nolan, 1998), favours 2–3°Tw caustic solution (0.9–1.35%) for lightweight fabrics and solution of 4–5°Tw (1.75–2.18%) for heavier material.

In textile practice, since the fabric selectively absorbs the chemical reagents, it is more usual to base quantities on the weight of material or o.w.m. For a kier, the volume of liquor is about three times the weight of goods (i.e. material to liquor ratio is 1:3).

A number of kier-boiling assistants are used to improve the scouring performance. The major role played by these agents is that of achieving good penetration of the fabric by alkali. An efficient wetting agent is essential. Turkey Red Oil (sulphated castor oil, anionic), once very popular, is now substituted by more efficient wetting agents, e.g. Dedanol OT/OTL (ICI) (non-ionic wetting agent), etc. Solvent-based detergents assist quicker removal of waxes, but they are not eco-friendly. Sodium silicate acts as a buffer and retains the removed impurities in the solution, preventing redeposition on the material.

The detailed recipes for caustic boiling for various qualities of cotton materials on the basis of industrial experience are given below (% on the weight of material or o.w.m.):

Caustic soda	X%
Soda ash	2%
Detergent	0.5%
Wetting agent (TRO, Dedanol OTL, etc.)	0.2%
Sodium silicate	0.5%
Sodium sulphite	0.5%

The quantities of caustic soda, suggested batch scouring machines and tentative scouring time are shown in Table 3.7.

*Table 3.7* Scouring conditions for different varieties of cotton fabrics

Fabric variety	Fabric weight (mts/kg)	Caustic soda (o.w.m) (%)	Time (h)	Machine
Lawn, voile, mulmul	15–20	0.5	4–6	Kier
Cambric, markin	12–14	1	6–8	Kier
Longcloth, poplin	8–10	2	8–10	Kier
Drill, rib, coating	6–8	3	10–12	Kier
Heavy-weight cotton	3–6	3	6–8	Jigger

*Note:* kiers operate at 30 p.s.i. steam pressure, jigger at boil.

Cotton check shirting and other fabrics with coloured threads may be scoured by open kier boil with 2% soda ash, 0.5% detergent for 8 h at 60°C.

Viscose fibre or fabrics may be scoured with 2 g/L anionic or non-ionic detergent for 1 h at 60°C.

Delicate fabrics are damaged while processing in kiers, while for heavier fabrics rope marks (i.e. coloured lines along the folds are visible after dyeing) may form. Heavier tubular knitted fabrics are largely scoured in winch or overflow dyeing machines just before dyeing.

### 3.10.1 Continuous scouring

Continuous scouring, either in open-width or in rope form, can be carried out with the aid of various machines. J-boxes were once very popular continuous scouring machines. Very large quantities of fabric are necessary to ensure the economic value of such processes, and it is preferable to have pieces of fabric of about the same width and weight stitched together. The large accumulation of fabric in rope form in the J-box implies that this technique can be used only for fabrics that are not very sensitive to creasing and brushing. The treatment with alkali in this machine is not under pressure; hence, a higher concentration of alkali will be required.

Scouring in J-box suffers from two disadvantages, namely:

1. High-pressure scouring is not possible in a J-box.
2. Tension required to take out fabric from the J-box may damage the material, especially in open-width J-box.

These shortcomings can be overcome by open-width roller steamer. In open-width roller steamer, the fabric is first padded through the scouring solution to at least 100% pick-up at 60°C with a running speed of 60 m/min, and then passed through a steamer at 100–110°C for about 30 s to 5 min. The fabric is then washed in an open soaper at 70–80°C with a counter-flow arrangement.

The advantages of rope processing over open-width are as follows:

1. Lower chemical costs
2. Higher production speed
3. Suitability for a wide range of fabric widths without stopping the plant
4. Efficiency and simplicity of the required equipment.

On the other hand, the advantages of open-width processing over rope processing are as follows:

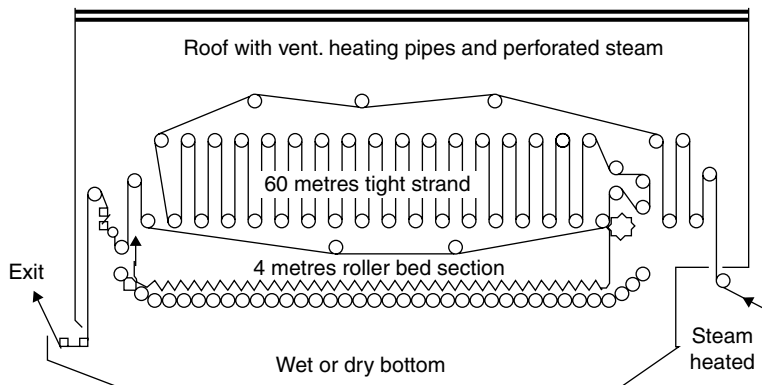
1. Suitability for fabrics sensitive to creasing
2. Better uniformity of treatment
3. Better warp tension control
4. Lower weft distortion and surface abrasion.

The choice between rope and open-width processes depends upon the nature of the fabric and its construction and upon production requirements. The open-width processes are preferred for heavier, higher-twist fabrics such as poplin, duck, twills and drills, in order to minimise wrinkles and crushing. The rope treatments are used for fabrics that do not have creasing problems such as knit-goods, sheeting, broad-fabrics, shirting, towelling and lining fabrics.

In the 1950s, two European manufacturers, Kleinewefer and Mather & Platt, developed Pressurelok and Vaporloc steamers respectively. The main difference between the two systems is the means of fabric transport. Kleinewefer used a tight-strand design while Mather & Platt used a roller bed system. The latter allows greater flexibility in running speed. The chamber is sealed along the top on both sides of a central beam. Each flexible seal is inflated pneumatically and presses on a low-friction covering. The pressure inside the seal is to be slightly greater than that inside the vessel. The continuous pressure steamer is used mainly for scouring woven cotton and polyester/cotton fabrics in dilute caustic soda solution for 2–3 min at 130°C (Park and Shore, 2004). The pressure system is excellent for caustic scouring, but not particularly advantageous for peroxide bleaching.

A major reason for the limited adaptation of continuous pressure processes was the development of good open-width processing at 100°C with short steaming times. The tight-strand steamers provided only a few minutes' steaming. The first atmospheric pressure horizontal roller-bed steamers provided only 3–5 min steaming at 60–80 m/min running speed. The horizontal roller-bed system was recognised as an excellent way to minimise warp and weft creasing, but memory creases especially on polyester/cotton fabrics occurred in early machines because of overtight packing, insufficient steam humidity control, inadequate pre-swelling of cotton or pre-setting of polyester. Most of the machines now include a tight-strand section, prior to roller-bed section, 'setting' prior to plaiting producing the best overall preparation conditions (Dickinson, 1984).

In continuous open-width atmospheric conveyor steamer, the impregnated fabric is plaited down onto conveyor belts for the required time and then taken to the washing section. Creasing is a problem in such systems;



3.4 Roller-conveyor combination steamer.

hence, recent installations are a combination of roller and conveyor systems commonly known as a combi-steamer (Fig. 3.4). The impregnated fabric in open width is guided over roller assembly for a time sufficient for swelling. After passing over this tight-strand roller section, the fabric is plaited down onto a roller-bed or conveyor belt with the fabric pile continuously moving so that the folds in the fabric are never long enough in one position for a permanent crease to form. The contact of the bottom of the fabric pile with each roller is also not long enough for drying to occur. A dwell time of about 6–20 min at 100°C is required for scouring of cotton fabric impregnated with 3–6% caustic soda. The production speed is around 100 m/min. This machine can be best utilised for combined scouring and bleaching.

Typical formulations and conditions for batchwise and continuous scouring processes reported elsewhere (Lewin and Sello, 1983) are shown in Table 3.8.

For polyester-cotton fabrics, the concentration of sodium hydroxide is to be reduced to avoid the risk of hydrolysis of polyester. The maximum allowable concentration depends on the cotton proportion of the blended fabric and the temperature and time of treatment. The addition of suitable scouring assistants is advised to compensate the reduction of alkali.

### 3.10.2 Scouring of knitted goods

The processing of knitted goods can be carried out in two forms: tubular or open-width (slit) form. In contrast to woven fabrics, knit-goods have a risk of distortion and the machine should put low tension on the fabric.

Pre-treatment of cotton knit-goods should remove 8–13% by weight of natural impurities (fats, waxes, etc.), as well as 1–5% by weight of impurities such as preparation and knitting oils. The soft handle of knit-goods should

**Table 3.8** Conditions for batchwise and continuous scouring methods

Batchwise machines →	Kier	Winch or jet	Jigger	Package or beam
Caustic soda solid (g/L)	5–10	5–10	5–15	15–20
Wetting agent (g/L)	0.5–1	0.1–0.2	0.5–1	0.5–1
Detergent (g/L)	0.5–1	2	4	2–4
M:L ratio	1: 3–5	1: 15–30	1: 2–4	1: 5–8
Temp. (°C)	130	95–98	95–98	100–130
Time (h)	4–6	1–2	2–4	3–5

Continuous machines →	J-box, conveyor, pad-roll	Open-width, atmospheric steamer	Pressure steamer
Caustic soda (% o.w.m.)	3–6	4–10	6–10
Wetting agent (% o.w.m.)	0.1–0.5	0.1–0.5	0.1–0.5
Detergent (% o.w.m.)	0.5–1	0.5–1	0.5–1
Temp. (°C)	100	95–98	130–140
Time (min)	30–120	10–30	1–2

be maintained. Hence, partial retention of natural fats and waxes without hampering absorbency is advantageous.

Knitted goods have certain advantages over woven goods. These are not sized, hence easier to prepare. As carded or combed yarns are used, knit-goods contain fewer seeds. The knitted fabrics allow better penetration of the liquor because of the low twist of the yarn and open structure of the fabric.

Knit-goods are pre-treated both in short and long liquor, continuously or discontinuously, in circular form, rope form or slit into open width. The breakdown of worldwide pre-treatment methods for knitted goods is reported as follows (Angstmann and Bradbury, 1998):

- (a) Discontinuous long liquor      60%
- (b) Discontinuous pad-batch        35%
- (c) Continuous                            5%.

Tubular fabric is first subjected to the process of reversing. The purpose of reversing is to avoid soiling of the face side of the fabric during processing and/or handling of the fabric.

For long-liquor batch process, after reversing the fabric is taken into a winch or overflow machine to carry out the processes of scouring, bleaching, dyeing and finishing. Unlike woven fabric, all the above processes for knitted materials are carried out in the same machine. The machine takes

about 6–8 h to complete all the processes. The material:liquor ratio for the winch machine is quite high. However, it is still preferred by small processors, as the initial cost of investment is low as compared to modern soft-flow or overflow dyeing machines suitable for knitted fabrics. Some of the known makers of modern soft-flow/overflow machines are Fongs, Tung Shing (Hong Kong), Thies, Then, Brückner (Germany), Sclavos (Greece), Hisaka (Japan), Brazzoli, ATYC, Belini (Italy), etc.

Overflow machines are of two types:

1. Workable under atmospheric pressure – suitable for cotton or acrylic up to 98°C.
2. High-temperature model for polyester and blend up to 140°C.

Such machines may be fully automatic or semi-automatic and operate mostly in rope form. Only a few models operate in sheet form. The machines are modular in construction, i.e. they are made of multiple expandable chambers or tubes called sections, each having a capacity of 100–125 kg.

The auxiliaries must not foam, so that they can be used in machines with high circulation and rapid movement of the fabric and have minimum impact on the environment. The key elements of the eco-profile provided by the European regulatory bodies are that the products should be APEO-free, have a BOD:COD\*100 ratio of more than 60% and bio-elimination (OECD or Organisation for Economic Co-operation and Development) should be greater than 70% (Angstmann and Bradbury, 1998). After wet processing and before drying, the knitted materials are subjected to hydroextraction, which is mostly carried out in centrifuge type of machine. However, the structure of the fabric may be distorted. The fabric must be subjected to detwisting before slitting, drying or calendering.

### 3.10.3 Solvent scouring of cotton

The wax content in grey cotton fabric reduces from 1.09 to 0.23% when treated with trichloroethylene for 15 s and to 0.15% after 30 s. Such treated material becomes absorbent on boiling, presumably because the quantity of residual wax is too small to reform a layer over the fibre surface.

In the solvent scouring process, the fabric in air-dry condition is run into a bath of boiling trichloroethylene for about 30 s and comes out through a solvent seal. The fabric is then passed through a second chamber, which contains water at about 90–95°C. The solvent-water azeotrope boils at 75°C. Hence, in the second bath, the solvent along with some water flashes off and is reused. The fabric emerges from this compartment through a cold water seal. Alternately solvent-treated material may be passed through a steam chamber. The solvent dewaxing process is particularly suitable for use

in conjunction with continuous peroxide bleach (Trotman, 1968). However, most of the solvents are toxic and not eco-friendly.

### 3.10.4 Bioscouring

During alkaline scouring, caustic soda not only removes wax but also leads to destruction of other primary wall components and even to some damage to the cellulose, causing high weight loss of cotton and decrease in strength. Environmental loads (BOD and COD) of effluent water are also higher. High amounts of salts are produced during neutralisation of alkali with acid. The alkalinity and salts are to be removed before dyeing by rinsing, demanding a large volume of water. Consequently, Total Dissolved Solids (TDS) in the effluent increases significantly.

For enzyme scouring, pectinase is the only enzyme needed for wettability/dyeability, while other enzymes may have beneficial effects. The process is most efficient when run at slightly alkaline conditions. The pectinase action does not create full wettability alone. Addition of auxiliaries is necessary.

The bioscouring process results in textiles being softer than those scoured in the conventional caustic soda process. However, the degree of whiteness is often less and seed coat fragments are not adequately removed. The most crucial factor in the whole bioscouring process is the removal of the enzyme-weakened cuticle compounds in the rinsing phase. Rinsing at high temperatures in the presence of surfactant and chelator is most efficient (Lenting and Zwier, 2002).

Pectinases and cellulases are very effective compared to the proteases and lipases. The change in water absorbency of cotton is rapidly catalysed by pectinases, cellulases or their mixtures. Pectinases can destroy the cuticle structure by digesting the inner layer of pectins in the cuticle of cotton. Cellulases can destroy the cuticle structure by digesting the primary wall cellulose immediately under the cuticle of cotton. Cellulases break the linkage from the cellulose side and pectinases break the linkage from the cuticle side. The result of the synergism is more effective scouring in both the speed and the evenness of the treatment. Physical destruction of cuticle was also revealed by scanning electron microscopy (SEM) photographs (Li and Hardin, 1997a).

Simultaneous desizing and scouring may be done by a combined enzyme system containing amylase, lipase and pectinase enzymes without the use of harsh chemicals (Karmakar, 1998).

Most of the enzymatic scourings did not give better results (Karapinar and Sariisik, 2004) than conventional alkaline scouring; however, the most similar results to alkaline scouring by means of wettability and pectin removal were achieved with combination of cellulase and pectinase and cellulose, protease and pectinase.

BioPrep 3000L (Novo Nordisk, Denmark) is an alkaline pectinase, free from cellulases (Lange, 2000). It works optimally at pH 7.0–9.5 and at temperature up to 60°C in exhaust systems and at somewhat higher temperature in pad systems.

The advantages of BioPreparation 3000L are (Lange, 2000):

- (a) Less caustic soda, acid, rinsing water and less energy for rinsing are required.
- (b) Mild alkaline condition is safer for blends with silk, wool, etc.
- (c) Cellulose structure and strength are retained.
- (d) Softer handle of fabric, less need for softeners.
- (e) Less weight loss of fabric.
- (f) BOD and COD in the effluent are 20–40% of those in the traditional process.
- (g) TDS is only 20–40% of that in the traditional process.
- (h) Combined processes are possible by combining various enzymes.
- (i) Non-corrosive conditions give a safer working environment and less wear of equipment.

The challenges of BioPreparation 3000L are higher whiteness, removal of seed fragments and development of a satisfactory continuous pad-steam process.

### 3.10.5 Efficiency of scouring

The main changes which occur in cotton goods during scouring process are as follows:

- (a) Loss in weight (about 5–10%).
- (b) Loss in length due to shrinkage during the boiling treatment.
- (c) Alteration in yarn count affected by both losses.
- (d) Changes in tensile strength (generally increase).

However, the most important characteristic of scoured fabric is increased and uniform wettability, which is necessary for subsequent processing. Wettability must be obtained not only in the capillary spaces between the fibres, but also inside the fibres themselves. While scouring is beneficial for wettability, when carried out in severe conditions it induces fibre deterioration, e.g. the creation of cavities in fibres or dissolution of the cuticle and primary wall.

Since the scouring treatment contributes to the dissolution of a portion of shorter cellulosic chains, it bestows on cotton a higher average degree of



polymerisation than that of native cellulose. Otherwise, the alkali treatment, in contrast to mercerising, does not induce any profound change in the fine structure of fibres.

The scouring efficiency may be tested in several ways namely:

1. Practical tests of absorbency
2. Measurements of
  - (a) Weight loss
  - (b) Protein content
  - (c) Residual wax content
  - (d) Methylene blue absorption (removal of pectic substances)
  - (e) Degradation of cellulose by various tests.

The scoured material is very clean in appearance. Hence, it is commonly said that ‘a good scoured material is half-bleached’. The whiteness achieved after scouring may be sufficient for dyeing in deep shades.

Absorbency may be assessed in various ways, the most popular being the ‘sinking time test’ (AATCC Test Method 17-1994).

The LINRA wipe tester is a more sophisticated test apparatus for fabric. In this test, drops of dye solution are applied to the test paper, which is drawn under the piece of fabric. The fabric is held in position for a certain time under constant load. Highly absorbent fabrics rapidly absorb the dye and very short streaks are shown on the paper. Poor fabric absorbency is shown up by long dye streaks being spread on the test paper. As with the drop absorbency test, sensitivity of the test can be modified by using dye solutions of differing viscosity.

During scouring, cotton material is liable to undergo oxidative degradation, leading to the production of oxycellulose having reducing aldehyde and keto group, and acidic carboxylic groups. Such reducing groups impart alkali sensitivity to cotton, especially at high temperature, with consequent lowering of tensile strength. The degradation may be assessed by determining any of the following (Roy Choudhury, 2006):

1. Copper number, a measure of the reducing groups present in cellulose.
2. Carboxyl group content.
3. Cuprammonium fluidity, which is a measure of molecular chain length of cellulose.
4. Tensile strength of the cotton material before and after scouring.

### 3.11 Mercerisation

Mercerisation refers to the treatment of cotton yarns or fabrics with caustic soda solution. Considerable quantities of cotton yarns and fabrics are

mercerised to improve lustre and/or dye uptake and more recently without tension to produce stretch materials. Cotton fabrics are mercerised in grey or bleached condition or after boiling off in alkali. Grey mercerisation is frequently practised to save on additional drying cost.

The objective of mercerising is to swell the cotton fibre, increasing its lustre, tensile strength (also retaining tensile strength after easy-care finish), dimensional stability and dyeability (in terms of uniformity and colour yield).

Traditionally, a cold solution of 25–26% by mass of sodium hydroxide is used, although better penetration and more even treatment is obtained with the more recent hot mercerising technique. The time of impregnation is rarely sufficient for maximum swelling, so that even with the mercerisation of bleached cotton, the addition of wetting agent is advantageous. Until recently, products based on cresylic acid (a mixture of *o*-, *m*- and *p*-cresols) were popular. Such products are toxic and non-biodegradable in nature. The biodegradable wetting agents include certain alkylarylsulphonates, some organophosphonates (e.g. sodium methyloctylphosphonate), alkylated diphenyloxide sulphates (e.g. dodecyldiphenyloxide sulphate) and especially sulphated aliphatic alcohols (e.g. 2-ethylhexyl sulphate). The most efficient sulphated alcohols are those with low molecular weight (chains with 4–8 carbons). Moreover, products with branched chains are more efficient than those with linear chains. A cresol-free alternative is sulphated 2-ethylhexanol, which is activated with about 10% butanol and unsulphated 2-ethylhexanol.

Some important observations about mercerisation are listed below:

- Maximum degree of mercerisation obtainable depends on the type of cotton and the growth conditions.
- Higher degree of mercerisation on cotton fibres having finer, uniform and circular cross-section such as Egyptian and North American varieties.
- For short-staple flat-type cotton, the effect is less pronounced.
- Mercerisation is most efficient after scouring and bleaching; owing to the absence of size on the fibre the used-up caustic solution is not contaminated with sizes.
- Mercerisation aids in removing crease marks for fabric bleached in rope form.
- Wetting grey cotton materials is not easy – a larger quantity of good wetting agent is necessary to assure uniform wetting.

When the aim is to improve dyeability only without much appreciable change in lustre, a less severe process called semi-mercerisation or causticisation is carried out. The treatment may be carried out with about 15% caustic soda with or without tension, as the shrinkage after the treatment is not very high.

The fabric after scouring is efficiently squeezed and with a water content of 60%, enters into a large caustic bath containing 300 g/L caustic soda in the usual process, or 530 g/L in addition mercerisation (Graif, 1996).

Yarns are mostly mercerised in warp form in a truly continuous manner or batchwise in hank form. Warp mercerisation is done in developed countries not only for warp yarn, but also for knitting yarn. The process ensures uniform mercerisation followed by uniform dyeing, though the lustre may be less than that obtained in hank mercerisation.

Mercerising ranges, for continuous mercerisation of fabric, consist of a sequence of machines for impregnation, penetration or stabilisation by passing over idling rollers, washing under tension, removal of alkali, neutralising, washing, squeezing and plaiting of fabric. Such ranges can be classified into three types as follows:

1. Stenter type or chain mercerising machine
2. Chainless mercerising machine with expander rollers for weft stretching
3. Chainless and padless mercerising machine where both impregnation and washing are done under tension.

The circular knitted fabrics can be mercerised in a tube mercerising machine having an adjustable circular expander.

### 3.11.1 Effects of mercerisation

#### *Increase in tenacity*

Mercerisation tends to increase the tenacity of cotton fibres. The changes in spiral angle and orientation are held responsible for that fact, but the explanation is controversial. The increase is also attributed to a strengthening of weak points along the fibre. The weak points include internal strains (spiral reversals), the places of low cross-sectional areas and the places of high distortions. The other important factors may be crystallite length and degree of crystallinity as well as the removal of cellulose of very low degree of polymerisation. With decrease in temperature, the increase in tenacity is more pronounced.

#### *Increase in lustre*

By applying tension during or immediately after caustic treatment, the fibres acquire a silky lustre – a valuable property of mercerised cotton. Due to the change from elliptical to uniform cylindrical cross-section

and untwisting of the fibres, mercerised cotton becomes lustrous, closely resembling cylindrical man-made fibres. The lustre depends on the quality of raw material. Long-staple fibre acquires a greater lustre than short-staple. Twisted double yarn becomes more lustrous than non-twisted loose yarn. When mercerisation is carried out without tension, no increase in lustre is observed. Most mercerising processes first allow the material to shrink in the alkali for better penetration, and then the tension is applied either before or during the removal of the caustic soda. To retain an optimum level of lustre, it is necessary not to release tension before caustic soda concentration is lowered to about 60 g/L. For this purpose, the first rinsing must be carried out under tension.

### 3.11.2 Other effects of mercerisation

- Considerable lengthways shrinkage occurs when fibres, yarns and fabrics are mercerised without tension. The fibre as well as yarn diameter, increases with corresponding decrease in metric count.
- On mercerisation, the convolutions or natural twists of cotton disappear and the morphological structure changes from twisted ribbon like structure to tubular.
- As the caustic concentration of 17.5% is the lowest at which any substantial increase in lustre was observed, Marsh (1979) concluded that the production of lustre is connected with the occurrence of uncoiling after or simultaneous with swelling.
- The characteristic hollow channel inside the cotton fibre or lumen almost completely disappears.
- X-ray examination of native and mercerised cotton fibres shows that a change in the crystal structure takes place, the original cellulose I being transformed to distorted crystal cellulose II on mercerisation. The comparison of unit cells shows that the planes carrying the long chains of  $\alpha$ -glucose residues have been moved apart due to mercerisation. The extent of conversion depends on the tension applied during the process. Mercerisation without tension causes complete transformation, while on mercerisation under tension, mixture of the two forms is found (Peters, 1967).
- Swelling with caustic soda reduces the degree of crystallinity from 70% to 50% when cotton is thoroughly mercerised. The reduction is slightly less for the treatment under tension. The size of crystallites also changes.
- The orientation of the crystallites, as measured by birefringence, changes little on mercerisation under tension, but significantly decreases under tensionless condition. The change may arise from changes in the spiral

angle of the fibrillar elements and not necessarily from changes in orientation of the crystallites within the fibrillar structure.

- Due to decrease in the degree of crystallinity, the resulting fibres have greater absorptive capacity and are more reactive to chemical agents, which manifest themselves in the acceleration of hydrolysis under the action of acids and damage by oxidising agents.
- Mercerised fibre is more resistant to light and weather effects than non-mercerised fibres.
- Mercerised material requires less dye to obtain the same colour strength than unmercerised material. The dye consumption is reduced by about 10–15% in light shades and about 25–30% in deep shades. The uniformity, purity and brilliancy of the shades are also higher due to the change of optical properties of the fibre by mercerisation.
- The dyes on mercerised materials are faster than those on unmercerised materials. This is probably due to swelling and opening of the structure with consequent higher penetration of the dyes.
- The temperature of mercerisation also has an influence on the crystalline structure of cotton. The cellulose I content and the total crystallinity index decreases with increase of temperature, whereas the cellulose II content follows an opposite trend.
- The elongation at break decreases and the Young's modulus increases significantly on mercerisation under tension. When mercerisation is carried out without tension, the value of elongation at break is three times the value of the unmercerised material, thus conferring elastic properties to cotton fibres. This elasticity is the basis of the preparation of stretch materials.

### 3.11.3 Hot mercerisation

Technically, hot mercerisation is carried out at 70–100°C for 4–60 s which leads to a uniform high swelling of cotton fibres with a softer feel. One process of hot mercerisation is to saturate cotton piece goods in caustic lye (50–58°Tw) for 5 s at 97°C under relaxed fabric conditions. The goods are subjected to controlled hot stretch after caustic saturation. The hot-stretched fabric is cooled under proper control below 25°C followed by successive tension-controlled washing called stabilisation (up to caustic soda concentration of 60 g/L) and washing under normal conditions.

### 3.11.4 Liquid ammonia mercerisation

Like mercerisation with caustic soda, ammonia produces changes in the structure of cellulose – reorganisation of the crystalline network with

cellulosic chains rotating and translating around their axle – giving a better accessible network to reagents.

The differences between the two types of mercerisation are as follows:

1. Penetration of ammonia into the fibre and its elimination are nearly instantaneous (between 15 and 25 s). Therefore, the treatment is very fast.
2. Ammonia is recoverable and reusable after a purifying distillation. Caustic solution after mercerisation, especially in grey form, is soiled and it creates pollution problems.
3. Water consumption is reduced to less than half in ammonia mercerisation.
4. Ammonia is a natural substance and the process may be considered as ideally eco-friendly.
5. It gives reagent-free textile goods.

The differences in fibre properties are as follows:

1. The properties provided by traditional mercerising (increased dye affinity and the change in appearance) are more or less preserved with ammonia. Improvements in lustre and dye uptake are, however, less than those of caustic mercerisation.
2. Ammonia, a weak alkali, does not damage the fibre in contrast to the very aggressive caustic soda. Mechanical properties like abrasion resistance, tensile and tearing strength are improved. Ammonia treatment increases tensile strength by 40% and the elongation at break by 2–3% of that of untreated cotton.
3. Less swelling by ammonia causes the fibre to become more plastic and malleable. The article life is increased and the new appearance is retained for a longer time. The difference in swelling also explains the more brilliant aspect of the fibre after caustic soda treatment and the satin gloss after the ammonia treatment.

In the Prograde process, developed by J. & P. Coats Ltd. (Scotland) in 1969, the yarn is passed through a liquor ammonia bath at  $-33^{\circ}\text{C}$  (contact time: 0.7 s) followed by a hot water bath (0.1 s at  $93^{\circ}\text{C}$ ), where it is stretched 10–30% as measured against ammonia-swollen length. The yarn is wound on a spool and dried continuously with hot air. The method, developed primarily for sewing thread, is claimed to be one thousand times faster than traditional yarn mercerising processes. Prior moisture treatment (up to 30% of dry weight) improves the effects, especially uniform dye pick-up.

The ammonia treatment on fabric is conducted continuously with lengthways tension. It consists of impregnation of goods with liquid ammonia at atmospheric pressure (i.e. at the boiling temperature of  $-33^{\circ}\text{C}$ ) followed by

the elimination of the reagent by evaporation (Sanfor-Set process), or by rinsing with water (Veramtex process).

In the Sanfor-Set process, the evaporation is done by passing over blanketed, steam-heated dry cans. The residual (5–10%) chemically bound ammonia is removed by light steaming. The Sanfor-Set or Duralized process combines liquid ammonia treatment and Sanforizing and is especially suited for heavy fabrics like denim and corduroy. The combined process is claimed to give enhanced dimensional stability, softness and smooth drying properties, with reduced seam puckering, edge fraying and leg twist in garment (Lewin and Sello, 1983). No strong alkali treatment should be carried out after ammonia treatment.

### 3.12 Preparation of proteineous materials

Animal or protein fibres contain a significant amount of non-fibrous impurities – about 50% in the case of wool and about 15–30% in the case of silk. These fibres are very sensitive to alkali and are damaged quickly on alkaline wet treatment at high temperature (especially wool). Hence, these fibres are scoured with large amounts of soap or detergent, with little or without alkali at low temperature. The time of treatment is also much shorter compared to that in the case of cotton.

### 3.13 Carbonisation and scouring of wool

Raw wool contains about 40–50% impurities. These include about 15–30% greases and suint, 5–20% sand and dirt, 1–10% VM – the relative quantities may vary widely. VM is removed by carbonising, whilst grease and suint are removed by scouring. The carbonising process consists essentially of the following stages (Park and Shore, 2004):

1. Impregnation of wool fibre with 5% sulphuric acid (96%) at 10–30°C
2. Drying at 100–105°C, followed by baking at 125–150°C for 1 min
3. Crushing through rollers to remove the charred debris
4. Neutralisation of the residual acid and rinsing.

Unlike raw cotton, containing wax, raw wool is greasy, difficult to spin and must be scoured before spinning. Good and careful scouring is important for subsequent processes, as greasy wool is more difficult to process. Although scouring of cotton in fibre form is done only for special purposes, the scouring of wool fibre is a standard and widely used process. Even if wool is already scoured in fibre form, additional mild scouring in yarn or fabric form is necessary to remove residual fatty matters and oils or lubricants added during spinning, knitting or weaving processes.

The fibre scouring process is quite troublesome as there are large amounts of impurities to be removed from a delicate fibre. Complete removal of wool wax is not desirable. The fibre should retain a small portion (between 0.4 and 0.6%) of the wool wax after scouring in order to avoid brittleness causing fibre breakage during subsequent spinning process. Sometimes spinners of woollen yarns prefer a residue as high as 3%. The feedback parameters of scouring are the residual grease content of the wool and the subjective assessment of quality – colour, brightness, felting, loftiness, etc. The efficiency of scouring is judged by measuring residual fatty matters in scoured wool. The disposal of highly contaminated waste liquor is much more complicated than that for cotton scouring.

Wool fibre scouring machines are of three types (Trotman, 1968):

1. Swing rake machine
2. Harrow machine
3. Paddle machine.

The first two are widely used in England, while the last one is a continental system for scouring shorter and dirtier wool. In the first two English methods, a number of prongs move the raw wool continuously through a series of shallow bowls or rectangular tank filled with the scouring liquor. Each bowl is fitted with a perforated false bottom over which the material moves. In the ‘swing rake’ machine individual prongs or rakes move separately and cause a greater degree of agitation.

In the ‘harrow’ machine the prongs are all mounted on one frame called a harrow and move together. This provides a comparatively gentle form of propulsion and is, therefore, particularly suitable for finer qualities of wool, which felts easily. Some systems of scouring raw wool of medium quality include both methods, first the swing rake and then the harrow.

In the continental method, the paddle gently swishes the wool along the bowl in which it has a longer period of immersion at a much lower temperature than in the English method. The continental system is a closer approximation to true emulsification. In the English method, the wool wax is partly removed by melting with subsequent wash. The English system operates at a temperature of 50–55°C for a total period of 10–15 min, whereas in the continental method the temperature is maintained at 28–38°C and the time of treatment is longer (20–25 min).

In all three systems, the wool is scoured in troughs or bowls with perforated false bottoms, which permit the heavy impurities to escape, by settling into the compartment at the bottom of the bowl. Side compartments are provided at the end of each bowl, to receive the liquor from the squeezing rollers. As the dirt settles and the fats float, the intermediate purer liquor



may be fed back into the bowl for reuse. All but the first bowl in a set are self-cleaning as above.

Wool scouring machines are generally made in standard widths of 28, 36 or 48 in and in lengths of 30–40 ft, to suit requirements. There are generally three or more bowls arranged in a line to scour the wool. Modern scouring machines designed for the middle range of Merino wool are typically six bowls long.

The dirty liquor from the first bowl may be taken to the centrifuge where cream, clear water and sludge are separated as top, middle and bottom layers respectively. The cream is treated with boiling water and is sent to the clarifier centrifuge for separating wool grease. The clear liquor after filtration may be sent back to the bowl, and sludge to the sludge-bed of effluent treatment plants.

From a chemical point of view, there are various methods of purifying loose wool and these are determined to some extent by the type of material to be cleaned, and the nature and amount of the impurities. The main methods of purification are as follows:

1. Emulsion scouring
2. Suint scouring
3. Solvent extraction
4. Freezing.

Wool wax is difficult to saponify under conditions that do not damage the wool fibres. However, it may be readily emulsified, particularly at a temperature that is slightly higher than its melting point (40–45°C). Emulsion scouring with soap is the most common method of cleaning loose wool. Scouring, most popularly known as ‘wool washing’, is done with 2–4% soap and 2% sodium carbonate, calculated on the weight of the wool. The melting point of the soap used for the scouring wool should not exceed 27–30°C. At present, wool scouring is most economically done with non-ionic detergents. A small amount of alkali may be beneficial for scouring, but no free alkali should be left on wool at the end of scouring. The temperature of treatment should not be above 52°C particularly when sodium carbonate is present. With sulphated alcohols, in the absence of alkali, the temperature may be allowed to rise to 70°C.

It is known that the potassium salts present in the impurities of raw wool and originating from perspiration possess detergency properties. The old-fashioned method of scouring wool is to steep it in water and use the liquor as detergent, often reactivated with lant or stale urine and pig-dung. The process generally operates in five stages:

1. De-suinting (16°C)
2. Grease removal with suint (60–70°C)

3. Rinsing (0.1% soap, 40°C)
4. Soaping (0.3% soap, 40°C)
5. Rinsing (0.1% soap, 32°C).

Organic solvents are used to extract wool wax commercially in Belgium and the USA. Though the process may not be eco-friendly and is costlier than aqueous scouring, the advantages are less felting and reduced entanglement of wool. Wool wax may be removed from wool by benzene, solvent naphtha or white spirit. Chlorinated hydrocarbon solvents are convenient, but usually cheaper petroleum solvents of high boiling point are used. Solvent and wax may be separated by distillation and the solvent reused.

A partial cleaning of wool is possible by freezing technique. A mild scouring is necessary after this treatment. When raw greasy wool is cooled to a temperature of  $-30$  to  $-45^{\circ}\text{C}$ , the fats freeze and become hard and brittle, but the wool fibre itself is not affected. After cooling for a sufficient time, it is subjected to vigorous agitation when the frozen grease breaks up into fine powder and falls away with a considerable quantity of vegetable and mineral matter. As VMs are removed largely during the treatment, 'carbonisation', i.e. the process of removal of VM, may not be necessary for most varieties of wool except fine felt wool.

### 3.14 Shrink-resist treatment for wool

While washing of woollen garments in aqueous media dimensional changes may occur because of relaxation shrinkage and felting of the fibres. Relaxation shrinkage is reversible and can occur in garments made from any fibre. Felting shrinkage is not reversible and is inherent to the wool fibre, largely associated with different frictional resistance in two directions (DFE) along the wool-fibre axis due to the scale structure of the fibres.

Most commercial shrink-resist processes control felting shrinkage by either modifying the scale edges to eliminate the DFE or by bonding the fibres together so that relative movement is not possible. Machine-washable wool garments are well established, particularly from knitted fabrics. Many commercial processes were developed, originally based on chlorination, although chlorinated residues are now most unwelcome from the environmental viewpoint. Fibre bonding is achieved by resin treatment, one of the most successful originally being Hercosett 125 (Hercules), a reactive polyamide-epichlorohydrin resin (Lewis, 1978).

The simplest sequence of pre-treatment of dry-combed or pre-scoured wool tops with a water-soluble, cationic polyamide-epichlorohydrin polymer Hercosett resin (Hercules) to prepare shrink-resist machine-washable wool in back washing machine is as follows:

- (a) Chlorination by applying sodium hypochlorite having 1.5–2.0% active chlorine on the weight of wool at pH 1.5–2.0.
- (b) Anti-chloring and neutralisation in the second bowl with sodium sulphite or metabisulphite and sodium carbonate or bicarbonate.
- (c) The Hercosett 57 resin treatment (5 g/L solid) in the third bowl at pH 7.5 and temperature 30°C.
- (d) The final bowl consists of a non-ionic polyethylene softener such as Alcolube CRT at alkaline pH.
- (e) Finally the tops are subjected to drying and curing (for resin).

Batchwise exhaustion techniques may also be followed.

Dichlorodicyanuric acid (DCCA) is one of the oldest chlorination reagents for imparting shrinkage resistance to wool by the Hercosett® shrink-proof process. Treatments with 5% DCCA applied at 30°C for 60 min from a citric acid buffered system, pH 4.0, followed by anti-chlorination with hydrogen peroxide or hydrogen bisulphite show small increases in alkali solubility and in bursting strength. Less than 2% chlorine is detected in 5 and 20% DCCA/anti-chlorinated spent baths. The 5% DCCA/hydrogen peroxide treatment improves shrinkage resistance by 54% and whiteness by 63% when compared to untreated fabrics (Cardamone *et al.*, 2004).

BASF proposed the use of quaternised resin, Basolan F, for both shrink-proofing of wool and for improving wet-fastness of anionic dyes, especially of milling and 1:2 metal-complex dyes. The process sequence is different to that of Hercosett. The wool top is chlorinated with acid hypochlorite, anti-chlored, rinsed and dried. The top is subsequently dyed and treated with 2–6% (o.w.m.) Basolan F resin at pH 7.0–8.5 with ammonium hydroxide at a temperature of 40–50°C for 10 min or by padding.

Most shrink-resist treatments are applied to wool tops, but wool knitwear is made shrink-resist by treatment with aqueous liquors in side-paddle and rotary-drum machines. Solvent techniques are also available. Traditional aqueous procedures are based on chlorination, using acidified sodium hypochlorite, but the rapid reactions of chlorine and hypochlorous acid with wool made the process difficult to control. Excessive oxidation led to dye decomposition, accompanied by wool yellowing and loss of strength. The chlorine generators commonly used more recently are alkali-metal salts of dichloroisocyanuric acid (DCCA), typified by Basolan DC (BASF). In acidic solutions these precursors are capable of liberating approximately 35% of their own mass as available chlorine. In the presence of wool, the salt may react directly with the fibre as well as being decomposed into chlorine and hypochlorous acid, which subsequently react with the fibre. Typically, wool is chlorinated with DCCA at pH 3.5–4.0 and a temperature of 20–25°C (Park and Shore, 2004). Chlorination treatments are now in decline for ecological reasons and chlorinated residues are unwelcome. Chlorine-free processes

have been developed to overcome these problems, based on the application of reactive pre-condensates which are subsequently polymerised on the fibre surface. Commercial processes are based on the use of Nopcolan SHR3 (Henkel) (Cockett, 1980a) and Synthapret BAP (BAY) (Cockett, 1980b).

Recently machine-washable wool is in high demand so as to avoid dry cleaning with chlorinated solvents such as perchloroethylene. So far wool top has been chlorinated for shrink proofing. However chlorination will be prohibited for Adsorbable Organic Halides (AOX) zero emission in the near future. Tahara *et al.* (2003) treated wool fibres and fabrics by pulse corona discharge, followed by two kinds of enzymes, protease and keratinase. It was found that the treatment of enzyme, in particular the keratinase, after the pulse corona discharge is very effective for shrinkage, weight loss and strength compared to the enzyme treatment alone. Scanning electron micrographs of wool surface after the treatment showed that the wool surface is treated uniformly with the enzymes, in particular the keratinase, after the pulse corona discharge, and the fibrillation of the fabrics reduces significantly. The dual treatment improves the shrinkage with little change of the strength and handle of the wool fabrics.

### 3.15 Degumming of silk

Silk is obtained in the form of a cocoon, an elliptical mass spun by silkworms. Perfect cocoons (uncut by the insect) are cooked in baths containing soap-soda, enzyme or water for mulberry silk and soda or enzyme for tussah and muga silk. The cooking bath may be an open single bath, three pan (bath) system, or pressurised vessel. A number of silk filaments are reeled together to form silk yarn.

Raw mulberry silk is white, golden yellow or yellow-green in colour, while wild silk is light to deep brown in colour. Raw silk does not possess the lustre and softness for which the fibre is known. The gummy substance called 'sericin' covers the fibrous material called 'fibroin'. The former imparts a harsh handle and must be removed in order to bring out the supple and lustrous qualities. Although both sericin and fibroin, the two components of raw silk, are protein, they differ considerably in their relative composition of various amino acids and accessibility. The process for removal of sericin is known as degumming, boiling off and less commonly scouring. Degumming of silk involves the cleavage of peptide bonds of sericin, either by hydrolytic or enzymatic methods and the subsequent removal of sericin from the silk fibroin. Since the sericin acts as a protecting coating in mechanical processes such as spinning, knitting and weaving, its removal is delayed until the completion of these mechanical processes, depending on the product. However, a slackened thin uneven structure of such degummed fabric is not acceptable in case of high-quality silk fabric. Hence, the recent trend is to degum

in yarn form followed by application of easily removable sizes, which are removed after weaving by desizing.

Degumming also removes accompanying substances like fats, oils, natural pigments and mineral components. Thorough and uniform removal of these impurities is important not only for uniform dyeing, but also particularly for good printing. Sizes must also be removed with some qualities (e.g., schappe). According to the origin of silk, its natural colour is very lightly to heavily marked (e.g. by chlorophyll, carotin). With some wild silk, this natural colouration may be very strong, often affecting the fibroin.

The main degumming agent is soap. Boiling off or degumming of silk is carried out just below boil (90–95°C) in soap solution with or without alkali according to the quality of the fibre. The removal is based on the water solubility and higher alkali sensitivity of the sericin as compared with the fibroin at pH values from 9.0 to *ca.* 11.5 (Sandoz, 1985). Some hydrolysis of sericin probably occurs. Stronger alkalis may attack fibroin. On the other hand, prolonged degumming time is required in the absence of alkali. During degumming, alkali is taken up by the sericin and the free acid from the soap is formed. This may be deposited on the fibre, reducing the rate of degumming and protecting it from hydrolysis. Alkali is often added to maintain or restore the pH of the bath, but it is rarely used alone, because it makes silk harsher in handle. For complete removal of sericin, sodium carbonate may be added. If the pH exceeds 11.0, the fibroin is attacked. Silk can also be degummed with strong acids – the gum is completely removed at a pH 2.5 after 30 min of treatment. However, acid degumming is not commercially successful. Protein-splitting enzymes are also able to degrade sericin.

The complete removal of sericin results in a considerable weight loss. Hence in certain varieties, the gum is not completely removed.

1. In ecreu silk, only 2–5% gum is removed; the object in this case is to extract the small quantity of wax that is present rather than to degum the silk. The handle of ecreu silk is relatively harsh, but even so, it is suitable for warp threads.
2. In souple silk about 8–15% gum is removed. Souple silk is fuller and softer in handle and is used for weft.
3. In cuite or boiled off silk the gum is completely removed.

During degumming process, care must be taken to avoid entanglement or fracture of the fine filaments, particularly while processing in yarn form. The mechanical stress on the silk is kept to a minimum during degumming so that the silk threads are not spliced. Severe and irreparable damage may be caused by mechanical treatments during subsequent dyeing and printing. To prevent surface rubbing and random movements, the material may be put into a bag. The machine should also have an extremely polished surface to

prevent fibre rupture due to abrasion. Similar to other animal products, silks of different varieties vary considerably in properties. The correct degumming method for each type of silk article should be carefully assessed. Improperly pre-treated silk may become yellow during storage under the influence of light. Four different degumming processes are used in practice:

1. Traditional method with soap
2. Degumming with synthetic detergents
3. Enzyme degumming
4. Acid degumming.

The acid degumming process has not been commercialised yet. However, it is claimed that the degumming at pH 1.0–2.9 with organic acids such as tartaric and citric acid gives a product with superior tensile strength to that obtained by soap degumming.

### 3.15.1 Traditional degumming with soap

The traditional method with soap is still the one mostly used, especially in China and India. However, slowly soaps are being replaced with synthetic detergents or enzymes. Exceptional soft handle is produced by soap degumming. But the treatment time is very long (2–6 h) and prolonged treatment may damage the material. Continuous processing of piece goods is hardly practicable. As soap is used, soft water is a decisive factor for good results.

The best soaps for degumming silk are made from olive oil commercially sold as 'Marseilles soap', which is now somewhat expensive. As a result, the less effective oleic acid soaps are being largely used. Tallow soaps are difficult to remove after degumming. Soap from cotton seed or coconut oil has been suggested, but they leave an unpleasant odour in the material.

The temperature of the degumming bath generally lies between 90 and 95°C; higher temperatures up to boil are apt to bring about some yellowing of the silk and inferior handle. A further difficulty of high temperature is that due to bubbling; the material is vigorously agitated leading to chafing and lousiness.

The addition of alkali to soap solution increases the rate of degumming and makes the process economical since the quantity of soap and time required are reduced. High-grade olive oil soap liquor gives a starting pH of 9.2–9.5, which rapidly falls to 8.5. The addition of alkali tends to maintain pH at the effective point. With up to 0.18% free alkali, no weakening of fibre occurs. However, the resultant silk acquires a yellowish tinge.

Mulberry silk is degummed for 2–6 h at 90–95°C in a bath containing 8–10 g/L Marseilles soap at pH 9.5 with soda ash. For schappe silk, the same boiling off bath may be used, but only for 1–2 h. The treatment is repeated in a second bath like the first one for 2 h, if necessary. The degummed silk is rinsed first at 50°C with ammonia and then rinsed twice, firstly at 40°C and then at cold.

A rapid method of degumming with soap is to treat for 1–2 h at 90–95°C at pH 9.5–10 in the following bath:

- 8–10 g/L Marseilles soap
- 1–2 g/L wetting agent
- 1 g/L soda ash
- 1 g/L sodium tripolyphosphate.

### 3.15.2 Degumming with detergent

Synthetic detergents are increasingly replacing soap, especially in Europe. Traditional degumming requires a huge quantity of soap, and pure soap itself is very costly nowadays. The use of soap also demands the use of soft water; otherwise a considerable amount of soap will be wasted by reaction with hard water. A variety of synthetic detergents is widely available and will be comparatively economical, as lesser amounts of synthetic detergent will be required. Moreover, the time of treatment is considerably shorter enabling continuous processing of piece goods. The synthetic detergent should be carefully selected since the same soft feel as that achieved with Marseilles soap is not always obtained.

A method recommended by Clariant (Sandoz, 1985) is as follows:

- The material is treated with 2.5–5 g/L Sandopan SRS liquid at pH 11.2–11.5 (with caustic soda) at boil for 30–120 min.
- The material is subsequently rinsed with water at 80°C. The processing may be discontinuous or continuous.

### 3.15.3 Enzyme degumming

This method is regularly used in China. The treatment time is somewhat longer than with synthetic detergent, but shorter than soap. It is considered to have a mild action on the fibres and is claimed to produce uniformly degummed material with soft handle and reduced lousiness. The recommended proteolytic enzymes are trypsin (of animal origin), pepsin and papain (of vegetable origin). They hydrolyse peptide bonds formed by the carboxyl groups of lysine and arginine. Enzymatic degumming is not a

single-step process. The gum must be swollen before the enzyme treatment. An additional treatment with mild alkali is necessary to remove natural wax, soil and lubricant oils.

Trypsin, a proteolytic enzyme secreted by the pancreas, is most active at pH range 7.0–9.0. Ammonium bicarbonate (0.1 mol/L) is considered to be a good buffer. For tryptic digestion, 1–2% enzyme on the weight of material at 37°C for 1–4 h is considered appropriate.

Papain, obtained from a vegetable source, papyrus latex, is most active at pH between 5.0 and 7.5 and at temperature of 70–90°C. Original poisonous activators potassium cyanide or hydrogen sulphide are being replaced with sodium thiosulphate, alone or an admixture with sodium hydrosulphide.

A bacterial enzyme, alkalase, is very effective in hydrolysing sericin. It may completely hydrolyse sericin in 1 h at 60°C and pH 9.

Clariant recommends the following steps:

1. Treatment at boil for 1 h with a liquor containing:
  - 0.5 g/L soda ash
  - 0.5 g/L Glauber's salt
  - 3 g/L wetting agent
  - 2 g/L sodium silicate.
2. Treatment at 40–45°C for about 1 h with another liquor containing:
  - 1–5 g/L protein enzyme
  - 1 g/L soda ash
  - 2 g/L Glauber's salt.
3. Treatment at boil for about 1 h in a bath similar to the first bath.

### 3.15.4 Degumming of wild silk

Wild silk, i.e. tussah (tassar) or eri silk, is obtained from wild surroundings (from forests without any sort of breeding or cultivation) and is naturally coloured pale brown to dark brown. It differs from mulberry silk both chemically and physically and hence its processing differs considerably. Generally, with tussah silk, the gum is not present in the same regular form as with mulberry silk. It is often embedded in the strongly fibrillated fibre and is therefore difficult to remove completely. However, very recently some new varieties of tussah silk have been produced mostly in China. These silks are very close in properties to the mulberry silk and they both can be processed in the same manner. In the conventional process the wild silk requires an initial scouring in a liquor goods ratio of 30:1 (minimum) and 10% (by weight of silk) soda ash. The temperature is raised to 40°C within 15 min, running the hanks vigorously initially and slowly later on. The bath becomes dirty brown. The hanks are treated for half an hour at 40°C when



about 10% weight loss occurs. The hanks are hydroextracted and entered in a fresh bath containing 10–15% soda ash at 45°C. The temperature is raised to 85–90°C in about half an hour and the treatment is done for 1 h. The hanks are washed and treated with 10% hydrochloric acid for 15 min, which brightens silk. The material is then washed well, soaped with 3–5% soap at 40–45°C for half an hour and again soured with hydrochloric acid. Souring may reduce strength slightly but elasticity and gloss improve considerably.

Tussah silk is often degummed in a bath containing 5 g/L Marseilles soap, 3 g/L non-ionic surfactant (fatty alcohol polyglycol ether), 3 g/L polyphosphate and 2–3 g/L soda ash (pH 9.5–10.0) for 1 h at 95°C. The treatment may be repeated or the materials may be further bleached with sodium hydro-sulphite (Das, 1992).

Silk may be degummed in the form of hanks or as hosiery or woven piece goods. The greater part of silk is treated in hank form. The machines and equipment should be appropriate for the particular physical form, as the silk material is very delicate and liable to be damaged even with little mishandling.

### 3.15.5 Degumming faults

One of the difficulties encountered in degumming is that the reagents not only remove the sericin and free parallel filaments of fibroin, but they also penetrate into the filaments. Due to an uneven structure, there is a danger of separating the fibrils. Further processing may break them, causing lousiness of yarn. The broken filaments are apt to be of a much lighter shade than the rest of the material after dyeing.

Improper treatments during processing may cause mechanical damage to silk. The silk threads may be very easily chafed (skin detachment) at the surface causing lighter shade after dyeing. The darker the colour, the greater the contrast becomes visible. The material may have a chafed surface or locally chafed marks, which appear like white particles, stuck to the surface.

### 3.15.6 Weighing of silk

Since silk is an elegant and expensive material, the substantial weight loss during degumming is compensated wholly or partially by a process called 'weighting'. The degree of weighting is normally expressed by a term par – 10% below par means 10% lighter than original silk, while above par means greater than original weight. More than 25% above par is common for neck-tie silk. Silk may be weighted up to 300% of its original weight.

Different substances and materials are used for weighting of silk yarns and fabrics, which can be broadly classified into three types, namely:

1. Vegetable
2. Mineral
3. Polymers.

Vegetable materials, namely tannins or special plant extracts (Persian berries), are hardly used today. Such weighting may be combined with dyeing by natural colour, such as logwood.

Mineral weighting with tin (IV) salt is still the classic method. Recently various polymer treatments have been developed by a number of research institutes. These weighting processes are mostly done by polymer grafting.

Some silk processors have adopted these methods especially for necktie silk. Experience has shown that up to 50% weight increase by grafting with methacrylic amide in the presence of ammonium persulphate showed no appreciable impairment of handle. The polymer treatment also modifies dyeing properties; hence it is not clear whether weighting should be carried out before or after dyeing.

### **3.16 Preparation of synthetic materials**

The various processing stages of polyester, nylon and acrylic fibres are described below.

#### **3.16.1 Heat-setting of synthetic fibres**

Unlike natural and regenerated fibres, the yarns and fabrics manufactured from synthetic fibres require a special preparatory operation called 'heat-setting'. During this operation, the material is subjected to thermal treatment under tension in hot air, steam or hot water medium. Unless this treatment is done, these materials will shrink when treated with hot aqueous solution in loose condition, and as a result the linear dimensions and the shape of ready-articles will change. The magnitude of shrinkage depends upon structural parameters such as orientation and crystallinity of the fibres, previous history of treatments and tensions applied, and external variables like temperature, time and tension applied during shrinking. The amount of thermal shrinkage exhibited by any particular fibre product reflects its history: the draw-ratio, the tension developed during other processes and any heat treatment that has been applied. Unset fabrics also tend to form creases, which are difficult to remove during subsequent processing.

The setting process releases the strains imposed during drawing, knitting or weaving processes, minimises creasing during wet processing and imparts a high degree of dimensional stability. In order to achieve a satisfactory degree of set in synthetic thermoplastic fibres such as polyester and nylon, it is necessary to supply sufficient energy to the fibre to weaken or to break interchain bonds and allow new bonds to be formed whilst the material is held to optimised dimensions. Thus the material must be heated to a temperature close to the thermoplastic point of the fibre and some degree of widthways or lengthways tension is normally imposed on the fabric.

The setting process consists of two stages (Rao and Gandhi, 1991):

1. Heating of the material to a specific temperature depending on the fibre type, ensuring breakage of intermolecular bonds and equalising internal stresses in chains.
2. Cooling of the material resulting in the restoration of intermolecular bonds, the fibre being in new state, free from internal stresses. The quicker the cooling and the lower the temperature, the better is the stabilisation effect.

The main techniques of setting are as follows:

- (a) Dry-heat setting (or simply, heat-setting/thermo-setting)
- (b) Steam-setting
- (c) Hydro-setting.

Dry-heat setting is generally carried out on synthetic fabrics in pin or clip stenter machines equipped with one or more heat-setting sections in which a temperature of approximately 170–230°C can be maintained either by indirect oil or electrical heating.

Steam- and hydro-setting are used mainly for setting of yarns such as nylon. Saturated steam as the setting medium is probably most widely used on garments, but is also applicable for certain types of knitted fabric. Steam-setting is carried out by using saturated steam at a pressure of 10–25 psi for nylon 6,6 and 5–15 psi for nylon 6. Flash heating of material is avoided as this can cause variation in dye affinity. The moisture in the steam is controlled within a small limit. The principal difference as far as the dyer is concerned is that the steam-setting reduces the rate of dyeing much less than that with dry heat-setting. On the other hand, the steam-set dyed fabrics have slightly less wash fastness than that of dry heat-set fabric. Since dry-heat setting reduces dyeing rate, small variations in heat-setting conditions gives rise to unevenness during subsequent dyeing, commonly known as ‘barré effect’.

Recently steam injection stenters have become increasingly popular. In these machines, high-pressure steam is injected and they offer the following advantages:

- (a) By expelling air from the setting chambers, the oxidative degradation, stiffening and yellowing of nylon is minimised.
- (b) The rate of heat transfer to the fabric is increased.
- (c) Higher setting temperatures can be attended without hampering fabric qualities; thereby the materials can be run at higher speed with shorter dwell period.

The lower temperature limit for heat-setting of polyamide and polyester is about 100°C. The lower the temperature, the longer should be the time of treatment. The substances (e.g. water) that promote fibre swelling loosen fibre structure by partial destruction of intermolecular bonds. Consequently, a lower temperature is required for steam- or hydro-setting than that for dry-heat setting.

Stabilisation is a reversible process. The greater the difference between the stabilisation temperature and the temperature at which it is to be processed, the higher will be its dimensional stability. The fabric may be subjected to setting at grey state, after scouring, after dyeing or during finishing. If heat-setting is done at grey state, less heating energy is required as the fabric is at dry state, while after scouring or dyeing the fabric is to be dried before heat-setting. However, during grey heat-setting, the impurities present in the fabric will be firmly embedded in the material and will be difficult to remove during scouring. The optimum conditions for setting various textile fibres in water, steam and dry-air are shown in Table 3.9 (Peters, 1967).

As compared to nylon and polyester, there is very little tendency for triacetate yarns to shrink on heat-setting. This means direct-contact heat-setting machines such as heated cylinders can be used to a greater extent for triacetate than for other synthetic polymer fibres.

*Table 3.9* Optimum temperature and time for setting of textile fibres

Fibre	In water		In steam		In hot air	
	°C	Min	°C	Min	°C	Min
Triacetate	–	–	–	–	190–220	0.5–2
Nylon 6	100	120–180	108–121	10–30	175–190	0.25–0.5
Nylon 6,6	100	120–180	115–130	10–30	190–215	0.25–0.5
Polyester	100	120–180	140	10–30	180–220	0.33–0.66

Steam and hot water can serve as excellent media for the setting of nylon as the setting can be achieved at significantly lower temperatures and consequently less fibre discolouration or stiffening occurs.

Polyester yarns are normally set by relaxation in saturated steam. Short-staple polyester yarns are commonly twist-set by steaming them whilst they are still on the spinner's ring tubes and the temperature should be restricted to 110°C to avoid distortion of the tubes. However, yarns with high potential shrinkage, such as ordinary polyester filament yarns, and yarn containing a component (e.g. viscose) that swells in the dyebath, must be heat-set before winding. Yarn steaming is carried out in an autoclave fitted with a vacuum pump, so that the chamber can be evacuated before and after steaming. Pre-evacuation aids the penetration of the yarn package by the steam. The sequence of evacuation–steaming–evacuation may be repeated. Polyester garments and hosiery can be stabilised by the above steaming process.

Different varieties of polyester fabrics are normally set by dry heat. The sequence, scour–heat-set–dye is the safest and most satisfactory for all types of goods. However, setting being in the central position of the processing sequence, the expense of drying will be higher as the fabric is to be dried twice.

For materials that are perfectly clean in loom-state, it is possible to use the sequence, heat-set–scour–dye. The sequence is very useful for warp-knitting industries. When heat-setting is a final process, as in the routine scour–dye–heat-set, the conditions of the setting may alter the handle of the fabric.

Clip stenters and pin stenters are used for heat-setting, but the latter are preferred for the purpose, because of their versatile dimensional control. The conditions chosen for stentering vary considerably between different types of polyester materials as shown in Table 3.10 (Rao and Gandhi, 1991).

The high thermal shrinkage of typical unset polyester filament materials leads to a thin and impoverished handle when high tension is applied. The best uniform finished effect is produced by restraining 4–5% of the potential shrinkage and by allowing an increasing degree of relaxation shrinkage to take

*Table 3.10* Heat-setting conditions for different polyester and blended fabrics

Type of fabric	Temp. (°C)	Time (s)
100% Polyester	180–220	20–40
Texturised	160–180	30
Polyester-cotton	190–210	20–40
Polyester-wool	170–190	30
Polyester-acrylic	190–200	30–60
Cationic dyeable	170–180	20–40

place in the stenter. Staple-fibre fabrics shrink less than filament fabrics. For worsted spun goods, 3–5% relaxation shrinkage is allowed in both warp and weft. The free weft shrinkage of a typical polyester-cotton shirting fabric is 4% at its normal setting temperature, but this is restrained by 2–3% to ensure the removal of creases and to gain control over weft straightness (Nunn, 1979).

When the uptake of disperse dyes by polyester materials being heat-set at increasing temperature is compared, it was observed that dye uptake decreases with initial increase in the heat-setting temperature. After reaching a minimum dye uptake, in the temperature range of 170–200°C, the dye uptake increases with further increase in the heat-setting temperature. The initial decrease in uptake may be due to lowering of amorphous volume per crystal as a result of parallelised chains coming closer in the amorphous region during formation of new crystals. In the later stages of crystallisation, the crystallites increase in size and become perfect. Consequently, the amorphous region per crystal increases. In the temperature range of 180–200°C, the dye uptake is less sensitive to heat-setting temperature. Hence, the variation in dye uptake due to local fluctuations of temperature will be lowest. Therefore, this is the most preferred temperature range for heat-setting of polyester materials.

Acrylic and modacrylic fibres cannot be heat-set in the conventional sense since the fibres are readily stretched or deformed at temperatures above approximately 75°C. A degree of stability, which is sufficient for practical purposes, can be achieved by passing such fabrics through a stenter at 120°C. Higher temperatures may be required while processing blends of acrylic or modacrylic fibres. Knitted fabrics produced from a feeder blend of acrylic and texturised polyester fibres, for example, are usually heat-set at about 160°C. Certain acrylic and modacrylic fibres are very sensitive to heat, and the temperatures above 120°C, or even lower temperatures, may cause discolouration if treatment time is lengthy (Cusack, 1975).

The handle of acrylics bears a greater resemblance to wool than that of any other man-made fibre. High bulk yarns, which have great appeal for certain purposes, can be made from polyacrylonitriles. When the fibres are hot-stretched, the whole of the elongation is not stable and, under the influence of steam, a relaxation of 15 to 20% takes place. Thus, if stretched and unstretched filaments or staple are spun together and subsequently steamed, one component will shrink and the other will not. This brings about a buckling effect in the non-contracting component, causing the yarn to increase considerably in bulkiness.

### 3.16.2 Scouring of synthetic fibres

The scouring procedures for synthetic fibres are relatively simple since the fibres contain fewer impurities, most of which have at least some degree of

water solubility, the most important being sizes and lubricants. The major sizes used are polyvinyl alcohol, carboxymethylcellulose and polyacrylic acid, all of which are completely or partially water-soluble.

### *Scouring of acetate fibres*

Secondary acetate and triacetate fibres can be scoured with soap or synthetic detergent usually at 60–75°C, this being sufficient to remove soil, oil, colouring impurities and any antistatic agents. Anionic synthetic detergents such as polyoxyethylene sulphates are preferred for scouring of all synthetic fibres that are to be subsequently dyed with disperse dyes, since non-ionic detergents with low cloud point may hamper stability of disperse dyes at high temperature. Addition of a sequestering agent will be helpful for hard water. In case of fabrics, relaxation of knitting or weaving tensions occurs during scouring under minimum tension at high temperature.

For acetate fibres, normally alkali should not be used as these ester fibres may be hydrolysed. The secondary acetate loses its lustre from excess alkali. A finish called 'S-finish' is applied on triacetate fibres in which the material is treated with 3 g/L caustic soda solution for about 1.5 h at 80–90°C (Nunn, 1979). The process reduces acetyl content of the fibre from its normal 62% to 59%. The saponification mostly occurs at the surface and thus gives rise to a thin skin. The advantages claimed are improvements in handle and drape, resistance to soiling and glazing-stiffening during ironing, antistatic properties, gas fume fading fastness, and wet and dry rubbing fastness.

### *Scouring of nylon*

Polyamide and polyester fibres are generally adequately scoured using an alkyl polyoxyethylene sulphate and sodium carbonate. For polyamides or nylons, non-ionic synthetic detergents (1.5–2 g/L) along with an alkali (0.5–1.5 g/L sodium carbonate or trisodium phosphate) are suitable. Anionic detergents such as fatty alcohol sulphonates behave like acid dyes and are adsorbed by the fibre. Their presence on the fibre will slow down dyeing and may reduce the exhaustion of the dyebath. If the material is to be dyed with acid dyes, a non-ionic detergent is to be used. Clariant recommends the use of crypto-anionic (i.e. anionic/non-ionic hybrid surfactants) ethylene oxide condensate or modified polyglycol ether with or without solvent. The presence of solvent imparts stain-removing properties. When scouring is carried out in jet-dyeing machines, low-foaming detergents should be used, as excessive foam generated would create problems in the subsequent dyeing process. When hard water is used for scouring, some salts of heavy metals may be retained by nylon fibres, presumably by combination with the free carboxyl end-groups, which the fibre contains. The temperature of scouring varies according to whether the material is already heat-set or not, being

70–80°C for the unset and 95–100°C for heat-set. High temperature may cause deterioration of the setting. For heavily soiled materials, scouring is preferably conducted before heat-setting in order to avoid ‘setting-in’ of the contaminants; however, the unset materials are prone to distortion and creasing.

If cationic spin-finish is present, the material is to be subjected to an acid wash at 50–60°C for 20 min with 1–2 g/L non-ionic wetting agent (e.g. Sandozin NIS, Clariant) and 1–2 mL/L formic acid (85%).

After scouring, the nylon fabric should be washed thoroughly before drying and heat-setting. Uneven drying after scouring and before heat-setting could lead to irregular results in dyeing, particularly with anionic product.

### *Scouring of polyester*

It is not always necessary to scour polyester fibre materials before dyeing. Loose stock, slubbing and some types of yarns are supplied in clean state and usually bear low quantities of processing aids which are compatible with disperse dyes. Such products can be simply washed with water or may even be allowed to remain in the dyebath. However, some products are heavily soiled, waxed or sized. Some may contain cationic processing aids. These must be removed before dyeing. If sizing agents are not removed easily, an additional step of enzymatic desizing is to be carried out. The processor should know the exact contaminants present and take appropriate action.

For most normal purposes, the scouring bath should have 1–2 g/L anionic synthetic detergent or soap (alone or admixture with non-ionic surfactant) and 2 g/L soda ash. For lightweight materials in rope form or unset filament materials, the temperature should be below 60°C. For other materials, scouring may be done at boil for 20–30 min or 4–5 ends in a jigger. For heavily soiled materials, the scouring time should be extended. Otherwise the soiled scouring liquor should be dropped and the process is to be repeated with a fresh bath. A soil-suspending agent such as sodium tripolyphosphate may be added.

The same conditions may be maintained for polyester-viscose blends. For blends with cotton and linen, the concentration of alkali should be doubled. For pad-steam or pad-roll processes of polyester-cotton blends, the padding liquor should contain 20–40 g/L soda ash and 5–8 g/L detergent. For heavier polyester long-staple fabrics or polyester-wool worsted fabrics, scouring may be done in rope form in a dolly or a similar scouring machine. The worsted fabrics require somewhat vigorous scouring than all-wool fabrics. The scouring may be done with 3–4% (o.w.m.) soap and 20–30 g/L soda ash at room temperature for 20–30 min, followed by rinsing at 40°C. The process may be repeated two to three times.

Nowadays some polyester fibres are subjected to ‘causticisation’ treatments with sodium hydroxide in the presence of a cationic surfactant to give



a lighter fabric with a silkier handle. The process causes localised saponification of the polyester surface.

### *Scouring of acrylic fibres*

For acrylic fibres, anionic surfactants should be avoided, because they may restrain the uptake of basic dyes. These fibres are scoured with an ethoxylated alcohol, either alone or with a mild alkali such as sodium carbonate or phosphate. The removal of lubricants (frequently anionic), oil and dirt prior to dyeing is recommended and sometimes essential. The best method depends on the type and quantity of substances to be removed. Sometimes a short cold rinse is sufficient. Usually a weak alkaline treatment with non-ionic detergent (0.5–1% o.w.m.) and ammonia (0.5–1% o.w.m.) may be carried out at 80°C. Phosphates can be used as an alkaline agent. After scouring, a thorough rinse at 50–60°C is necessary to remove any residual alkali.

## **3.17 Bleaching**

After desizing and scouring processes, the textile materials are in a very absorbent state. Some materials may still have a yellowish or brownish colour, which may affect the tone and brightness of the shade obtained by dyeing, particularly for light shades. For white goods, the whiteness requirement is much more stringent. Whiteness of scoured goods is far below satisfactory because of the presence of residual colouring matters. The quantities of such materials are normally very negligible but they are firmly embedded into the textile materials. Their removal requires a special step of preparatory process called 'bleaching'. The main object of bleaching is the removal and/or destruction of natural and adventitious colouring matters with the production of pure white materials. The natural colouring matters present in various textile materials are different. The same bleaching agent may be used for a number of textile fibres, though the conditions and the extent of bleaching required may be different in different cases. For example, Egyptian cotton is darker in colour and more difficult to bleach as compared to American varieties. One must be careful when choosing the bleaching agent as the textile material may be damaged by the bleaching agent, particularly under certain pH range and temperature.

In a broader sense, the term 'bleaching' encompasses a series of operations designed to produce a clean, white material including three distinct processing stages, namely desizing, scouring and whitening.

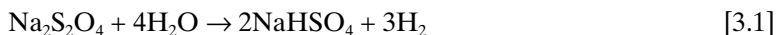
Cotton contains portions of the husks of the cotton ball, called motes, which are trapped between the cotton fibres during picking. Caustic scouring softens, decolourises and erodes these particles, allowing their removal during the washing operation following scouring and bleaching; other particles are simply bleached and remain in place.

Bleaching agents convert coloured impurities into colourless particles. Colour is imparted by a chromophore, i.e. a moiety usually involving alternating carbon-carbon single and double bonds. Bleaching destroys these double bonds by addition (saturation) or rupture. Once the free electrons of a double bond are tied by substitution or by rupturing the double bond, electromagnetic radiation is not absorbed and is reflected in the visible region of the spectrum and colour ceases to exist.

### 3.17.1 Reductive bleaching agents

Many colouring matters can be reduced to colourless compound by reducing agents. However, on exposure to air and sunlight, the reduced colourless components may be oxidised and the yellowish tint reappears.

As sodium dithionite is available in solid form, it is more convenient to transport, store and handle compared to gaseous sulphur dioxide. Sodium dithionite is reasonably stable, provided it is kept in dry and cool surroundings. When acting as a reducing agent in aqueous solution it is converted into sodium bisulphate.



The best bleaching action is obtained at 50°C at a pH of 7.0. The solution is very unstable unless the pH is above 10.0. However, excess caustic soda may convert it into sodium sulphide and sulphite.



Animal fibres, wool and silk can be bleached with 4 g/L sodium dithionite at 40–50°C in the absence of any metal other than stainless steel. Iron or copper salts, if present, will be reduced to their respective sulphides causing greyish colouration of the substrate, which is very difficult to remove. The bath is allowed to stand for 4–6 h, after which the material is rinsed thoroughly. Wool reductive bleaching is mostly carried out with stabilised dithionite at pH 5.5–6.0.

### 3.17.2 Oxidative bleaching agents

Oxidative bleaching agents are much more effective than reductive bleaching agents. In the past, people used to carry out dew bleaching of cotton and linen goods utilising atmospheric oxygen. Slow atmospheric oxidation is not commercially viable. Hence, a number of chemical oxidation processes are

being utilised for bleaching of various textile fibres. The most important oxidative bleaching processes are as follows:

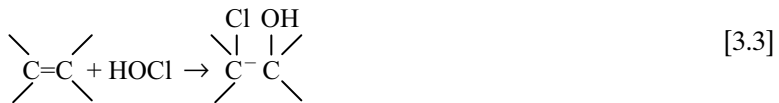
1. Hypochlorite bleaching
2. Hydrogen peroxide bleaching
3. Sodium chlorite bleaching.

### 3.17.3 Hypochlorite bleaching of cotton

Hypochlorite bleaching is a low-cost process using simple chemicals. The process was once very popular, but is now being phased out because of the following disadvantages:

1. It is not eco-friendly since it releases effluent of high AOX value. It is therefore banned in many countries.
2. There is a risk of fabric damage if the pH is low.
3. The process is slow and is to be carried at low temperature. Hence, it is difficult to carry out as a rapid continuous operation.
4. There is a chance of yellowing of bleached fabric on storage.
5. It releases relatively high concentrations of salt in the effluent process water, which is objectionable from an ecological point of view.

Two chemical compounds are utilised in hypochlorite bleaching – bleaching powder and sodium hypochlorite. The bleaching mechanism with chlorine-containing compounds is based on saturation or rupture of double bonds. The first mechanism is hydroxychlorination to a chlorohydrin (Equation [3.3]), the second mechanism is chlorination to form 1,2 dihalide (Equation [3.4]) and a third mechanism involves oxidation by electrophilic substitution, which destroys carboxyl chromophores (Mock, 1985).



The hypochlorite bleaching process has declined considerably due to ecological problems. When bleaching small quantities in long liquor (material:liquor [M:L] ratio about 1:5), a solution containing 1.5–2.75 g/L of available chlorine may be used for a treatment time of 2 h. However, for a

circulating system as above, the M:L ratio may be as low as 1:1 and the available chlorine falls rapidly in the early stages. A liquor containing 8–10 g/L of available chlorine may be used in such cases and the circulation may be continued for 6–10 h.

After bleaching with bleaching powder, some calcium carbonate, formed by reaction of calcium hydroxide with atmospheric carbon dioxide, is deposited on the material. Hence an after-wash with mineral acid, termed 'souring', is essential to remove such deposits. The same treatment is also used for removal of residual chlorine after sodium hypochlorite bleaching. The material is finally washed to remove traces of acid, which may otherwise form hydrocellulose.

The material is to be thoroughly washed before acid treatment. Generally, a treatment time of 30 min to 1 h with 1% sulphuric acid at room temperature is sufficient.

A better method for removal of residual chlorine, particularly after bleaching with sodium hypochlorite, is to treat the material at 40°C for 15 min in liquor containing 2–2.5% (o.w.m.) a reducing agent like sodium sulphite, bisulphite, hydrosulphite or thiosulphate.

### 3.17.4 Peroxide bleaching of cotton

Cotton bleaching today usually means hydrogen peroxide treatment, since hypochlorite and chlorite methods have lost ground because of their adverse impact on the environment.

Hydrogen peroxide, although costlier, has several advantages such as:

1. Universal bleaching agent: It can bleach most of the textile fibres without damaging the materials.
2. Eco-friendly: As the decomposition products of hydrogen peroxide are oxygen and water, bleaching can be safely carried out in an open vessel. No AOX is generated even in the presence of salts.
3. Permanent whiteness: It does not react with proteins. Hence, a permanent whiteness can be achieved without preliminary alkali treatment.
4. Combined scouring and bleaching: Since peroxide bleaching is conducted under alkaline conditions at or near boil, it is the only bleaching agent that can be used for the combined scouring and bleaching process.
5. Versatile bleaching processes: It allows versatile processing such as batch or continuous, hot or cold, rapid or long dwell.
6. Better fabric appearance: As peroxide bleaching is carried out at or near boil, the broken seed or other VMs are removed during the treatment and consequently the cloth appearance after bleaching is much better and fuller than hypochlorite bleached material.

7. Less tendering: In hydrogen peroxide bleaching there is little risk of tendering due to over-bleaching.
8. Bleaching of coloured goods: Vat-dyed coloured goods can be safely bleached with hydrogen peroxide.
9. No after-treatment: No souring or any other after-treatment is necessary.
10. Compatibility: It is compatible with most dyes and fluorescent brightening agents (FBAs).

The difficulties of peroxide bleaching are as follows:

1. Instability: Hydrogen peroxide solution is unstable at high alkalinity and in the presence of metallic impurities.
2. Stabiliser: Hydrogen peroxide ensures whitening in conditions where it is rather unstable. Hence, a stabilising agent must be used which regulates the release of oxygen which has no bleaching power and which may cause fibre damage. Sodium silicate, though a most widely used stabiliser, is liable to deposit on the fabric and on the equipment. However, a number of water-soluble biodegradable organic stabilisers are now available in the market.
3. Process control: The use of multiple chemicals needs careful control.
4. Cost: The process is comparatively expensive.

The presence of natural impurities during peroxide bleaching is advantageous as they exert a stabilising effect upon hydrogen peroxide, preventing excessive loss of oxygen. Earlier it was thought that prolonged alkali boil is necessary for removal of wax so that the cotton materials become absorbent. However, recent studies show that for imparting absorbency it is not necessary that the wax be completely removed. The rupture of the primary cell walls of the cotton fibre, where wax is situated, may be sufficient to impart absorbency. The presence of hydrogen peroxide in combined processes accelerates rupture of cell walls. Hence, the absorbency is attained much quicker than separate scouring and bleaching processes. Since desizing may be carried out with hydrogen peroxide, it is possible to combine desizing, scouring and bleaching in one procedure.

The strength of peroxide solution may vary widely and is expressed in terms of the volume of available oxygen liberated from one unit volume of the liquor. Thus if 1 mL of solution liberates 1 mL of oxygen at Standard Temperature and Pressure (S.T.P.), the solution is equivalent to one volume solution. The relationship between volume strength and percentage composition of hydrogen peroxide is shown in Table 3.11.

At present it is more common to express strength by percentage weight of hydrogen peroxide. Textile bleaching grade hydrogen peroxide is mostly of

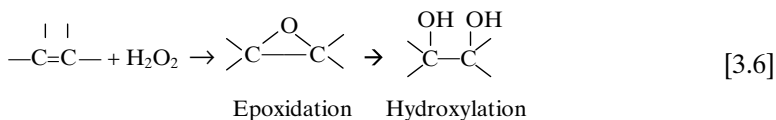
**Table 3.11** Relationship between volume strength and % strength of hydrogen peroxide solution

Volume strength	% Strength
1	0.3
10	3.0
100	27.5
131	35
197	50

27.5 and 35% strength. The strength of hydrogen peroxide can be measured by titration with N/10 potassium permanganate in the presence of an acid.



In peroxide bleaching, the carbon-carbon double bond is destroyed by epoxidation and hydroxylation (Equation [3.6]) (Mock, 1985):



Earlier bleaching action of hydrogen peroxide was thought to be due to the liberation of nascent oxygen, but this explanation is no longer valid. Under certain conditions, particularly with regard to pH, hydrogen peroxide decomposes into hydrogen and perhydroxyl ion ( $\text{HO}_2^-$ ), which is thought to be responsible for bleaching action. However, further research (Mock, 1985) has strongly favoured the presence of superoxide radical anion ( $\bullet\text{O}_2^-$ ). Hydrogen peroxide solutions normally require the addition of an activator to bring about bleaching. The most common activator is alkali, which presumably encourages the formation of the perhydroxyl anion; this then reacts further with hydrogen peroxide to give the superoxide ion Equation [3.7].



Alkalinity favours the liberation of perhydroxyl ions, i.e. the rate of forward reaction is increased due to neutralisation of  $\text{H}^+$  ion released forming water ( $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ ). However, excessive alkalinity causes the peroxide to become unstable.

Bleach activators like anionic nonanoyloxybenzene sulphonate (NOBS) and cationic tetraacetylenediamine (TAED) (Shao *et al.*, 2010) and

N-[4-(triethylammoniomethyl)-benzoyl]caprolactam chloride generate peracids allowing bleaching at lower temperature and at reduced time, resulting in savings in energy and reducing fabric damage. The last one was found to be superior to the anionic activator in bleaching under hot conditions (Lim *et al.*, 2004) as well as in cold batch process (Gürsoy *et al.*, 2004).

Hydrogen peroxide is decomposed catalytically by traces of many metals such as copper, iron, manganese, chromium, etc., and their oxides. This is accompanied by increased degradation of cellulose. In the presence of catalysts, the alternate reaction takes place evolving oxygen. The liberated oxygen has no bleaching power.



With increase in temperature, the stability of hydrogen peroxide decreases. For natural and man-made fibres, the time of bleaching will be too long unless the temperature is higher than 80°C. In practice, the treatment is conducted at 90–100°C for 1–1.5 h, but in a pressurised vessel the temperature may also be raised to 120–130°C, with a reduction in treatment time as short as 20 min. The evolved oxygen accumulates at the top of the enclosed vessel, which can cause tendering of the material due to oxycellulose formation at high temperature.

The catalytic effect of metal ions is not limited to the decomposition of hydrogen peroxide. Simultaneously the fibres are attacked, DP and the tensile strength decrease considerably. Localised concentration of the catalyst accelerates the oxidation of the fabric to such an extent that ‘pinholes’ or ‘razor cuts’ are formed in the fabric. These are due to local dissolution of the cellulose of very low DP values (Lewin and Sello, 1984).

Stabilisers are necessary to slow down the decomposition of both hydrogen peroxide (Equation [3.8]) and the active bleaching agent. The most common stabilising agents have been the colloidal sodium silicates. The formulae of silicate are best represented in terms of the ratio of sodium oxide to silica, as in sodium metasilicate ( $\text{Na}_2\text{O}:\text{SiO}_2$ ) and orthosilicate ( $2\text{Na}_2\text{O}:\text{SiO}_2$ ). These silicates, however, are in crystalline form in which the ratio is 1 or greater. In the colloidal forms originally preferred for peroxide bleaching the ratio is less than 1, e.g. alkaline glass (1:2) or water glass (1:1.6 to 1:1.38). The colloidal silicates are efficient and economical stabilisers, but care is needed to ensure efficient washing-off in order to avoid deposits of silica on the fabric and equipment. The stabilisers work as buffer and sequestering agent for transition-metal ions, e.g. iron (III) and copper (II), which would otherwise catalytically degrade the hydrogen peroxide. A small quantity of magnesium salt must be present if sodium silicate is to act as a stabiliser. Hard water having, at least, 2° hardness will

usually supply the need. If soft water is used, 0.1–0.2 g/L magnesium sulphate is to be added. Insoluble silicon compounds may be precipitated in the package dyeing machine. To avoid such precipitation, additional alkali may be added to bring the ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  to around 2.25:2.75. To avoid a risk of degradation of the cellulose, a mixture of sodium hydroxide and sodium carbonate is used as alkali. Water-soluble impurities in raw cotton can have a considerable stabilising effect on hydrogen peroxide solution. It is, therefore, preferable to bleach unscoured cotton, unless the material is heavily soiled. Theoretically, sequestering agents should be the best stabilisers – the various types of sequestering agents used in textile processing are as follows:

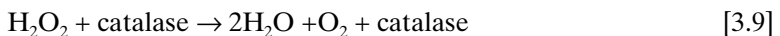
1. Polyphosphates
2. Polyhydroxy-carboxylic acids
3. Aminopolycarboxylic acids
4. Phosphonic acids
5. Polyacrylic acids.

It is important to recognise that whilst transition-metal ions catalyse the destruction of peroxide, the alkaline-earth element stabilises it. In the absence of calcium and magnesium, even silicates cannot act as bleach stabilisers (Shore, 1990).

Clariant developed a new organic stabiliser called Stabiliser SIFA (Fornelli, 1994), the main features of which are as follows:

- (a) Perfect stabilisation of hydrogen peroxide under severe conditions, i.e. long steaming times (20–30 min) of a non-scoured fabric as in the case of a continuous combined scouring-bleaching process.
- (b) It is bio-eliminable and phosphate-free.
- (c) Progressive whiteness – the degree of whiteness of cotton rises along with increasing concentration of the stabiliser.
- (d) Stabiliser SIFA exercises a strong influence on the effect of optical brighteners.
- (e) Sodium silicate can be replaced entirely, thereby avoiding deposition problems.
- (f) Stabiliser SIFA inactivates the metal cations (iron ions), thus preventing undesirable decomposition of peroxide and damage of material.

A trace amount of residual hydrogen peroxide (several ppm) can cause dyeing problems. The advantage of catalase enzyme as a ‘peroxide killer’ is that it attacks only hydrogen peroxide and nothing else. The reaction is as follows:





Normally, when using catalase, the number of rinses after bleaching can be significantly reduced.

Since cotton is a natural fibre, it is not a uniform material in its physical dimensions, chemical constitution or even in colour. Metals such as Ca, Mg, Fe, Cu and Mn are present in varying quantities in cotton fibres of different origin. High metal content of textile materials can lead to a lower level of whiteness, unacceptable level of strength loss and in the worst case, pinholes in the prepared fabric. Acid desizing may be useful in these cases.

Hydrogen peroxide is an active bleaching agent for cellulosic fibres under alkaline conditions. However, excessive alkalinity will cause instability and decomposition of hydrogen peroxide with liberation of oxygen. In order that bleaching is completed within a reasonable time, it is necessary to adjust the pH of the bleaching liquor to between 10.0 and 10.5 for cotton. For cotton, generally a mixed alkali of sodium hydroxide and sodium carbonate is used.

Hydrogen peroxide bleaching may be carried out as batch process in kier, winch or jigger machines, as semi-continuous pad-batch process or as continuous pad-steam process.

#### *Batch (exhaust) processing*

A general guide recipe for bleaching of unscoured cotton and cotton-polyester blends in a winch machine or any other long-liquor machine (M:L ratio 1:10–20), is as follows:

Sodium silicate (79°Tw)	7 g/L
Sodium hydroxide	0.5 g/L
Sodium carbonate	1.8 g/L
Hydrogen peroxide (35%)	1–2 g/L
Wetting agent	As required
Temperature	90–95°C
Time	1–2 h

#### *Semi-continuous process*

The recipe for padding liquor may be as follows:

Sodium silicate	20 g/L
Caustic soda	5 g/L
Soda ash	5 g/L
Hydrogen peroxide (35%)	5–10 g/L
Wetting agent	As required

After padding cotton or other cellulosic goods may be stored (covered with a polyethylene sheet to avoid evaporation) at cold or in a hot chamber for 12 h. The whiteness is not as good as kier-bleached material, but may be sufficient

for dyeing pale or bright shades, or for the materials, which may be damaged on boiling with aqueous solution. Residual peroxide remaining in the spent liquor can be activated by 1% soda ash or caustic soda solution at 80–90°C.

It is well known that peracids, such as peracetic acid, show stronger oxidative bleaching than hydrogen peroxide but there are potential safety problems for both storage and use. Using peroxide-activator such as TAED, it is possible to bleach cotton by cold pad-batch process. The optimised quantities reported are as under:

30 g/L hydrogen peroxide (30% w/w), TAED: hydrogen peroxide:: 0.25:1 to 0.33:1, 3 g/L sodium hydroxide, 6 g/L sodium silicate and 6 g/L wetting agent. The optimised batching time is 5–6 h (Shao *et al.*, 2010).

### *Continuous processing*

Continuous peroxide bleaching processes were developed as a cost-effective alternative to hypochlorite in the late 1930s using a first in, first out system, called a J-box. J-boxes are primarily used for rope form. J-boxes were slowly phased out because of a number of inheriting problems like creasing in rope form and excessive tension on the fabrics.

The open-width bleaching processes are of particular importance for polyester-cotton blends, which are very sensitive to creasing. In spite of high energy consumption and chances of uneven heating, these machines have revolutionised bleaching processes as treatment time has been brought down very significantly. The scouring and bleaching recipes for cotton fabrics in three continuous steamers having varying dwell periods are shown in Table 3.12 (Mahapatro *et al.*, 1980).

Most of the recent installations are a combination of roller-conveyor steamer (Fig. 3.4). The saturator or impregnator device is an extremely important part of a continuous bleach range. It must evenly and rapidly

**Table 3.12** Cotton scouring and bleaching recipe for three types of continuous steamers

Chemicals (g/L)	Dwell time in the steamer (min)		
	20–30	10–15	2–3
<i>Scouring</i>			
Caustic soda	20–30	30–40	80–100
Scouring aid	3–8	5–10	10–15
Wetting agent	2–3	2–3	2–3
<i>Bleaching</i>			
H <sub>2</sub> O <sub>2</sub> (35%)	20–30	30–40	40–60
Sodium silicate	5–10	12–15	15–20
Caustic soda	4–6	5–7	6–8
Wetting agent	0.5	0.5	0.5

impregnate the fabric with the treatment chemicals. The most common open-width impregnator is a single box with four or six dips and nips before final squeezing to the desired wet pick-up. Two-stage impregnation units force initial impregnation into the fabric using a roller nip with maximum load being about 400 N/cm (50 kg/cm or 280 lb/in.) of bowl width, i.e. about 10 tons, across the total width and a second series of dips before expression with a nip pressure half of the above, i.e. 5 tons.

Modern bleaching ranges operate with a maximum wet-on-wet application of 150% giving residual liquors of less than 10 litres. The pre-treatment cycle is considerably simplified and the quality of bleaching goods and operating reliability is improved. The basic logic is simple: the higher the application value, the more efficient the bleaching effect. Maximum application is the new state of the wet-on-wet impregnation. A number of maximum impregnation systems have been developed recently. A few systems developed in Germany (Fornelli, 1994) are as follows:

- Booster and BEN-IMPACTA systems (Benninger AG)
- Flexnip system (E. Küsters)
- Dip-sat Varic system (Max Göller)
- Raco-Yet system (Ramisch Kleinewefers)
- Super-Sat system (Babcock)
- Optimax system (Menzel).

All these ranges have a common function, i.e. maximum application of the bleaching liquor during impregnation of the goods before steaming. They all prevent creasing and chafing in the steamer and make alkaline scour boiling unnecessary. A shorter production cycle means higher final quality.

For continuous processing of knit-goods, J-boxes are no longer in use. Several other machines have been developed, such as spiral winches, Galaxy (Brückner, combination of a J-box and flattened open-width tube), Uni-Wash washer (Aroili), Spray-TEX jet washing unit and Traflo-TEX suction drum washer (Babcock). The actual bleaching in the last two machines is carried out in a reservoir called a Store-TEX unit (Meyer, 1999).

### 3.17.5 Combined scouring and bleaching of cotton

The advantages of combined processes are increased production with reduction in labour cost and reduced treatment time and lower consumption of water, steam and electricity. The loss in weight and strength of material is also less. The disadvantage is increased chemical cost as a higher dose of hydrogen peroxide is required. The declining price-rates of peroxide with increasing cost of utilities may make the process more economical.

In the presence of hydrogen peroxide, the scouring process is accelerated and less time is generally required to achieve good absorbency of the material.

A guide recipe (% o.w.m.) for combined scouring and bleaching in a kier is as follows (Trotman, 1968):

Magnesium silicate	0.05 g/L
Sodium silicate	2–3%
Caustic soda	0.3–0.8%
Soda ash	0.6–1.0%
Hydrogen peroxide (35%)	3–5%
Wetting agent	As required

For a closed kier, the temperature may be raised to 110°C. The bleaching is continued for 1–3 h. For an open kier, the time required may be 5–8 h. Instead of caustic soda and soda ash, caustic soda only (0.6–1.4%) may be used.

A very popular machine for carrying out combined scouring and bleaching of lightweight woven fabrics is the high-capacity (300–500 kg/batch) jumbo jiggers. The trough of the jumbo jiggers may be V-shaped or rectangular to accommodate very thick cloth-wound rollers.

The recipe recommended for jigger machines (Lewin and Sello, 1984) is as follows:

Sodium silicate (79°Tw)	4–10 g/L
Sodium hydroxide	1–1.5 g/L
Sodium carbonate	1.8 g/L
Hydrogen peroxide (35%)	1.5–3.5 g/L
Wetting agent	As required
Temperature	80–100°C
Time	1–3 h

### 3.17.6 Chlorite bleaching of cotton

Sodium chlorite has several advantages as a bleaching agent such as:

1. Bleaching without scouring: As the bleaching is conducted under acidic condition, white cellulosic goods can be bleached without scouring to retain natural oils and fats and thereby, natural softness. The weight loss is also low.
2. High whiteness, low degradation: Under recommended conditions, high whiteness is achieved without degradation of cellulose.
3. Bleaching other than cotton: It can be applied not only on cotton but also on many other fibres and their mixtures such as on rayons requiring milder bleaching and for synthetic fibres like polyamide and polyester.

4. No problem with iron stain: Traces of irons do not catalyse bleaching reactions and do not bring about degradation of cellulose.
5. Mild rinsing: Rinsing after bleaching is simpler since no fibre-substantive alkali is used as in case of hypochlorite and peroxide bleaching.

However, sodium chlorite is very corrosive for the equipment. It is, therefore, necessary to use ceramic, plastic or special steel equipment for this bleaching process. Normal stainless steel equipment is to be used with enough precautions and with certain corrosion inhibitors. Stainless steel containing 2–5% molybdenum in addition to the normal content of 18% chromium and 8% nickel may be used following certain precautions. The resistance depends upon the formation of very fine surface films of metallic oxides. The surface irregularities may cause local breakdown of the protective film and a well-polished surface is of utmost importance. Occasional pacification can be made by treatment with 10–20% nitric acid for 10–30 min. The treatment may be made after every fourth to sixth bleaching. A stainless steel plant will be serviceable for an almost indefinite period if chlorite and peroxide bleaching processes are carried out alternately or even if peroxide bleaching is carried out occasionally.

Chlorite bleaching is to be carried out in a closed vessel with tight sealing of the equipment and good ventilation is to be maintained in the bleaching room since noxious chlorine dioxide evolves during bleaching.

Sodium chlorite is a medium-strength acid and hydrolyses in water to a limited extent (Lewin and Sello, 1984). It is only active in acidic solution. Chlorous acid decomposes into chlorine dioxide, chlorate, chloride and oxygen in acidic solutions:



The reactions depend on the pH. Above pH 5.0, the solution decomposes slowly and at pH above 7.0 it becomes virtually stable. Below pH 5.0, the decomposition mainly produces chlorine dioxide and chlorate. A small amount of chlorine dioxide is decomposed into chlorine and oxygen. Chlorine dioxide is believed to be responsible for bleaching. Liberation of chlorine dioxide should be controlled and should be equal to the rate at which it can be consumed by the impurities in the cotton.

Between pH 2.5 and 3.5, the liberation of chlorine dioxide would be more rapid. The optimum condition for bleaching of cotton is at pH 4.0 at a temperature of 85–95°C for a period of 30 min to 6 h. The concentration of

required sodium chlorite is 5 g/L in long liquor, 20–30 g/L in pad-batch process and 70 g/L in continuous units like the J-box.

Organic acids such as formic or acetic acid are preferred as activator instead of corrosive mineral acids. Various sodium salts such as sodium dihydrogen phosphate, disodium hydrogen phosphate, disodium pyrophosphate, tetrasodium pyrophosphate, sodium formate and sodium acetate can be used as buffers. The phosphates exert a protective action against the corrosive effect of chlorine dioxide on stainless steel. Various compounds, which hydrolyse in hot aqueous solutions such as diethyl tartrate and ethyl lactate, can be used as activators for pad-steam as well as long-liquor batch processes. Ammonium chloride, sulphate and its aliphatic carboxylic acid salts may also be used. The evolution of chlorine dioxide will be slow (causing less environmental pollution).

Sodium nitrate is also effective as a protecting agent or corrosion inhibitor. Some commercial inhibitors are based on inorganic fluorides. They act as a buffer at pH 4.0 and suppress the evolution of chlorine dioxide.

For bleaching in package dyeing machines or in winch, the composition of the liquor may be as follows:

2–4 g/L	Sodium chlorite (80%)
1 g/L	Sodium dihydrogen phosphate
1–2 g/L	Sodium nitrate
1–2 g/L	Wetting agent and required amount of formic acid to bring pH to 3.8–4.2.

After running for 10–15 min cold, the temperature is raised to 80–85°C and maintained for 1–2 h. This is followed by soaping and washing.

Knitted cellulosic goods are generally not sized. Such materials can be lightly scoured with 4–5 g/L soap or 2 g/L synthetic detergent and 1 g/L soda ash at boil for 30 min and then bleached with sodium chlorite in a winch machine with a liquor containing:

1–3 g/L	Sodium chlorite (80%)
1 g/L	Sodium dihydrogen phosphate (anhydr.)
1–3 g/L	Sodium nitrate

The goods are allowed to run in this liquor for 5–10 min, after which sufficient formic acid (about 0.5–1 g/L) is added to bring the pH to between 3.8 and 4.2. The temperature is gradually raised to 80–90°C at which it is maintained for 1.5–2.5 h. The pH is to be checked from time to time and adjusted if necessary. The process is very suitable for white goods, as natural softness will be retained due to light scour. If the goods are to be dyed, a subsequent antichlor treatment is to be carried out with 0.5 g/L sodium bisulphite and 0.1–0.2 g/L formic acid for 15 min at boil.

### 3.17.7 Peracetic acid bleaching of cotton

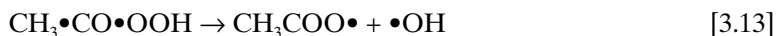
In recent years, peracetic acid, i.e. acetyl derivative of hydrogen peroxide, has come into use for bleaching, particularly of synthetic fibres:



The more concentrated the acetic acid, the greater will be the yield of peracetic acid. About 1% sulphuric acid acts as a catalyst when the yield of peracetic acid increases significantly.

Peracetic acid is available as a clear, colourless, fairly stable solution of 36–40% strength. Highly concentrated solutions are difficult to handle, as the acid is volatile and has a pungent irritating smell, although not toxic compared to chlorine dioxide.

A free-radical mechanism cycle can be assumed for peracetic acid decomposition in the bleaching bath, the perhydroxyl radical acting as an active bleaching species. The radicals are formed according to the equation below:



The stability of peracetic acid is not quite as high as that of stabilised hydrogen peroxide. To avoid damage to the cloth in the presence of ions such as copper and iron, a sequestering agent (e.g. diethylenetriamine-penta-acetic acid) may be added. Other stabilisers of peracetic acid are sodium hexametaphosphate and sodium pyrophosphate.

Oxidoreductases, enzymes that catalyse oxidation or reduction reactions, may find use in enzymatic bleaching process. Although some degree of colour removal is possible through the use of selected enzymes, seed coatings remain a severe problem.

For cotton fabric, optimisation of bleaching with peracetic acid was carried out on the basis of degree of whiteness, loss of DP, weight loss and economic considerations for bleaching of cotton fabric with peracetic acid. The stated optimum conditions are as follows:

- Concentration: 15 g/L of 15% peracetic acid
- Stabiliser: 3 g/L sodium hexametaphosphate
- pH value: 7.0
- Temperature of treatment: 70°C
- Time of treatment: 60–70 min.

The degree of whiteness is comparable with that obtained with sodium hypochlorite. The fibre damage is less and AOX value (chlorine-containing compound) is low (Hickman, 2002).

### 3.17.8 Bleaching of jute

Although jute fibres contain considerable amount of impurities, jute materials are generally bleached without prior scouring due to their alkali sensitivity. Jute differs from linen in its high lignin content (about 11–12% dry weight). The lignin, together with hemicellulose, provides intercellular binding material known as middle lamella, holding the fibres together. In contrast to linen, it is neither desirable nor necessary to delignify jute. Jute is effectively bleached by hydrogen peroxide while most of the lignin remains.

A consequence of the presence of lignin in bleached jute is that its whiteness is not fast to light and there is gradual reversal to the original colour (photo-yellowing). Though the best varieties of jute are sufficiently white to allow dyeing without bleaching, it is difficult to achieve light-fast dyeing in pale and medium shades. The presence of ultraviolet (UV) radiation in sunlight in the range of 330–370 nm causes yellowing. Lignin breaks on UV exposure, leading to the formation of orthoquinones and other chromophores (i.e. chemical groups that absorb visible light resulting in colour sensation) (Chattopadhyay, 1998).

Generally jute is bleached in two steps: chlorite bleaching followed by peroxide bleaching. Sodium chlorite is suitable for bleaching and delignification of jute. It removes more lignin than hydrogen peroxide. Treatment of jute fabric with acidified 4% (o.w.m.) sodium chlorite solution, pH 4.0–4.5 at 90°C for 90 min, improves the whiteness of the materials.

The bleaching with hydrogen peroxide causes a markedly lower loss of weight of jute (10% as against 17.9% in chlorite bleaching according to one unpublished study) and a slightly lower loss in strength. A typical recipe for bleaching jute with hydrogen peroxide in a jigger (% o.w.m.) is as follows:

3–6%	Hydrogen peroxide (50%)
6–8%	Sodium silicate
0.5–0.7%	Caustic soda
0.2–0.5%	Non-ionic detergent
0.05%	Chelating agent
pH	11.0
Temperature	80–85°C
Time	2 h

After bleaching with hydrogen peroxide the fabric should be thoroughly rinsed with hot and cold water, followed by a treatment with 2–3 g/L acetic acid. The brightness of peroxide bleached jute material was found to increase when pre-treated with an enzyme mixture containing cellulase and xylanase.

Jute fabrics can be bleached effectively with peracetic acid in the presence of tetrasodium pyrophosphate. A buffered medium is essential during bleaching in order to achieve fibre brightness (Cai and David, 1997).



### 3.17.9 Bleaching of flax

The preparation of linen is a compromise between the whiteness level desired (often defined in quarter steps up to full white) and the loss in mass tolerated. The presence of residual woody debris (sprit) may be desirable in certain end-uses or tolerated for low loss in mass. In such cases, careful dye selection is necessary to give uniform coverage. High whiteness demands multiple-step processing and there is a danger of separating the fibre bundles, called cottonisation. The risk of this fault is minimised by repeated mild treatments rather than one severe stage (Park and Shore, 2004). Reductive scouring of linen with alkaline dithionite has been advocated before oxidative bleaching (Abou-Zeid *et al.*, 1991). The traditional lime boil and hypochlorite bleach has been abandoned in favour of chlorite or peroxide bleaching (Sloan, 1997). Detailed studies of optimised bleaching conditions for chlorite, hypochlorite or peroxide treatment have been carried out to ensure their utilisation in the most effective manner with respect to the functional characteristics of the linen. The scope for bleaching linen will be restricted to peroxy chemicals if chlorine-containing bleaching agents are eventually withdrawn from use on the grounds of AOX formation. It has been shown that peracetic acid is an effective replacement for both bleaching and delignification (Hickman, 1994). Mercerising of linen enhances the quality of the fabric. This treatment can be given on a jumbo jig following scouring and bleaching. Mercerising does not improve the lustre but it strengthens the fibres at their nodal points, increasing the abrasion resistance by about 30% (Sloan, 1997).

Linen or flax is bleached either as yarn or in the form of cloth. Usually there is no difficulty in making linen materials absorbent, because the rate at which linen absorbs water is significantly greater than that for cotton or viscose. This has been attributed to the presence of nodes in the fibre.

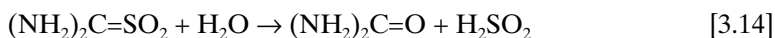
Unlike cotton, flax contains a small amount (about 2%) of lignin. This component may be bleached with sodium chlorite or with hypochlorite under acidic conditions, after which the lignin may be dissolved in dilute alkali. For bleaching of yarn in a package dyeing machine, a scour is given with 8–10% o.w.m. soda ash at a temperature of 95°C for 2 h. The yarn, after thorough hot and cold wash, is treated with 4% sodium chlorite solution at 80°C for 45 min maintaining pH of 3.8–4.2.

The yarn is then treated with 0.5% (o.w.m.) hydrogen peroxide along with soda ash and sodium silicate at 80°C for 60 min. The chlorite bleaching, followed by peroxide bleaching, may be repeated for a second time if required.

## 3.17.10 Bleaching of wool

Before the invention of hydrogen peroxide, sulphur dioxide was the only bleaching agent for wool. Woollen goods were exposed to sulphur dioxide in an enclosed chamber and the process was known as 'stoving'. The goods were scoured and hydroextracted, and in wet condition hung on wooden poles inside a chamber. The goods were slightly alkaline before the treatment, since under acidic or neutral condition there was very little bleaching. At the end of treatment, the material was treated with 1–2% of sodium sulphite at 40°C. The residual sulphur dioxide was converted to sodium bisulphite, which was readily removed by washing.

Sulphur-containing bleaching agents (e.g. sodium dithionite) may damage cystine groups of wool. A safer and effective reductive bleaching agent is thiourea dioxide,  $(\text{NH}_2)_2\text{C}=\text{SO}_2$ , which can be applied at pH 7.0 at 80°C for 2 h. A sequestering agent must be included in the bath, to prevent metal-catalysed decomposition of this reductive bleach. It has less effect on the physical properties of the fibre than other reductive bleaches. The active bleaching species in thiourea dioxide bleaching is sulphinic acid.



Arifoglu and Marmer (1990) described a novel oxidative-reductive bleaching system, which involves first bleaching with hydrogen peroxide for 60 min at 60°C and then adding thiourea, adjusting pH to 4.5–5.5 to generate thiourea dioxide 'in situ'.



The reduction bleaching is carried out with thiourea dioxide, thus generated for 25 min at 60°C followed by washing.

However, this method may cause considerable wastage of reducing agent due to large excess of hydrogen peroxide usually left in the bleach bath. Moreover, thiourea (not thiourea dioxide) is classified as carcinogenic.

In an alternative method, after peroxide bleaching, organic catalysts are added to decompose the residual peroxide. Iron or copper salts may cause excessive damage and discolouration of wool, while  $\text{Co}^{2+}$  is the only cation reported to cause no damage or discolouration. Thiourea dioxide or methane sulphinate is then directly added to the bath with necessary pH adjustment.

Thiourea may be replaced with trisodium salt of trithiocyanuric acid (TTCA, *s*-triazine-2,4,6 trithiol, i.e. three sulphur ions on the carbon atoms of the triazine ring). It is not carcinogenic, but more expensive than thiourea (Marmer et al., 1993).

Approximately 10% of total world production of wool is bleached, although it is difficult to quantify the amount of top-up bleaching in the last scouring bowl. The wetted wool carries the hydrogen peroxide added to this bowl to the dryer, where most of the bleaching takes place. Hydrogen peroxide is virtually the only oxidative bleaching agent for protein fibres like wool and silk. Hypochlorites have poor bleaching action and give rise to yellow colouration and seriously tender wool in alkaline solution.

Sodium chlorite gives a pinkish white shade, which requires after-treatment with sodium bisulphite.

For wool and other protein fibres, the control of alkalinity is most important as high alkalinity may cause breakdown of polypeptide chains with consequent loss in strength. The minimum alkalinity required to activate hydrogen peroxide is sufficient to damage the fibre if the temperature exceeds 60°C. The recommended pH is 8.0–8.5, which is much lower than that maintained during cotton bleaching. Degraded wool fibres, such as chlorinated wool, are more sensitive to alkali.

If the woollen material contains traces of metals like iron and copper, there will be immediate tendering of the material. Adding sequestering agents in the bleaching bath can eliminate the action of metallic catalysts. Under damp and slightly alkaline state, mildew and enzymes may develop on the materials. Some of the enzymes also cause rapid decomposition of hydrogen peroxide. The micro-organisms can be destroyed by passing such materials through a solution of hypochlorite having available chlorine less than 40 ppm.

The rate of decomposition of hydrogen peroxide, and hence the rate of bleaching can be retarded by stabilisers and accelerated by activators. The most important function of the stabiliser is to maintain the internal pH of the fibre, irrespective of the pH of the liquor, between 8.0 and 8.5. As far as the buffering is concerned, sodium silicate and non-silicate mixed stabiliser are the best. With sodium pyrophosphate, there is a tendency for the solution to decrease in pH during bleaching from the adjusted pH value of 8.5. With trisodium phosphate, on the other hand, there is an increase of pH value depending on its concentration.

The compounds that increase pH values, such as sodium carbonate and ammonia, can be used as activators. Higher alkalinity is harmful for wool, whereas low alkalinity will slow down the bleaching process. The alkalinity should be checked periodically and adjustments made if necessary.

Batchwise bleaching may be done in a tank composed of stainless steel, ceramic or wood. No direct contact of material should be made with the steam coil. Wool may be bleached with 0.3–1.2% (w/w) solution of hydrogen peroxide depending on the whiteness required, the discolouration of wool and the time permissible to complete the bleaching. The bath may be prepared as follows:

Sodium silicate	7 g/L
Soda ash	2 g/L
Hydrogen peroxide (35%)	3–6 g/L
Wetting agent	As required
pH is adjusted to 8.5–9.0	

or

Tetrasodium pyrophosphate	2 g/L
EDTA (30%)	1 g/L
Hydrogen peroxide (35%)	2–4 g/L
Wetting agent	As required

The temperature of the bleaching liquor can be constantly maintained at 50°C and the material is allowed to stand for 4–16 h. Recent optimisation is intended to reduce bleaching time to an hour. For overnight bleaching, the initial temperature should be 54°C and may be allowed to drop to 40°C by the next morning. A very large proportion of unused hydrogen peroxide remains in the spent liquor (as high as 90%) and should be reused. The material after bleaching is passed through a squeezing roller from which the expressed liquor returns back to the tank.

After bleaching under alkaline condition, a good rinse with weak acid solution (1 mL/L acetic or formic acid) is desirable. Wool that is slightly acidic retains whiteness better during drying.

Less degradation of wool occurs when it is bleached under acidic conditions. The method can be synchronised with the scouring of loose wool. After passing through the scouring bowls, the fibres travel through a bowl made of stainless steel containing 0.5–4 volumes of hydrogen peroxide. The liquor may be made up with:

Formic acid	1.2 mL/L
Hydrogen peroxide (35%)	2–4 g/L

The pH is adjusted to 4.0–4.5 with formic acid or soda ash. After squeezing, low cross-bred wool should retain 4–5% of its weight of hydrogen peroxide (35%). For better quality of wool, the retention of only 1.5% is sufficient. After bleaching, the goods may be dried immediately, but ageing for 12–24 h is preferred. No bleaching takes place before the wool is placed into the dryer where the water is evaporated, leaving the peroxide behind. Bleaching occurs over the subsequent few days. Acid bleaching is particularly suitable for blankets.

Levene (1997) studied ‘bio-bleaching’ of wool under both oxidative and reductive conditions. The studies showed that hydrogen peroxide bleaching in the presence of protease preparation, Bactosol SI (Clariant),

considerably improved whiteness and hydrophilicity. Alkaline proteases with improved stability to peroxide have been subsequently prepared such as Durazyme 16.0L (Novo Nordisk). The enzyme treatment may be carried out for 1 h at 50°C and pH 9.0. The bath was cooled to 45°C before adding hydrogen peroxide and ammonia to pH 8.5–9.0. The addition of the protease enzyme (about 0.5–1%) shortens bleaching time by half for the same whiteness. Similarly, an appreciable increase in whiteness can be achieved under reductive conditions by treating wool with the protease papain, applied in the presence of a mixture of sodium bisulphite and sulphite at pH 6.5–6.9.

Some wool fibres, such as Karakul or Canary, are heavily and non-uniformly pigmented. Heavily pigmented or naturally discoloured animal fibres are bleached by ferrous mordant method which is a delicate and risky wet operation. The pigmented wool is first treated with a solution of iron (II) sulphate, rinsed and finally bleached with hydrogen peroxide. The presence of iron (II) ions in the melanin pigment causes hydrogen peroxide to undergo radical decomposition, leading to oxidising species that are far more aggressive than the perhydroxyl anion. These radicals bring about not only a complete disruption of the melanin pigment, but are also very efficient in the decolourisation of the dye formed (Berek, 1994).

### 3.17.11 Bleaching of silk

Bleaching of silk with hydrogen peroxide can be carried out in more severe conditions than wool, since silk is not easily degraded. The material is to be carefully checked for metal spots, which may cause catalytic degradation of hydrogen peroxide. Most varieties of silk are bleached by steeping, but winch machines may be used for fabrics. The treatment is carried out with 0.55% w/w hydrogen peroxide solution made alkaline with sodium silicate and ammonia to give a pH of 10.0, or with addition of tetrasodium pyrophosphate and EDTA at 60–75°C for 2–4 h. For overnight steeping, the concentration of hydrogen peroxide may be reduced. Over-bleaching should be avoided as yellowing may occur. An alternate recipe for mulberry silk is as follows:

Hydrogen peroxide (35%)	15–20 mL/L
Stabiliser Awni (Clariant)	0.5 g/L
Imerol XN (Clariant, wetting agent)	2 g/L
pH 9.0 with trisodium phosphate	

The material is immersed at 40°C and treated at 90°C for 1–2 h, then rinsed with hot and cold water.

For tussah silk the recipe is as above, but with 20–30 mL/L hydrogen peroxide (35%). The treatment time is 4 h or more. If the tussah silk has strong

self-colour, the material is treated for 30 min at cold with 2–3 g/L potassium permanganate.

The material is then treated for 45 min at cold in a fresh bath containing:

Sodium hydrosulphite	15–25 g/L
Sulphuric acid (conc.)	0.4 mL/L

The material is thoroughly washed with hot and cold water.

With tussah silk it is often impossible, depending on its origin, to attain the same degree of whiteness within a single piece or from piece to piece. As goods of similar whiteness cannot be obtained, it is advisable to check the pieces well and classify them in different processing categories.

### 3.17.12 Bleaching of synthetic fibres

Acetate fibres are usually sufficiently white and require no bleaching, unless very bright pastel colours are to be dyed or a 'super-white' material is required. Hydrogen peroxide or peracetic acid may be used at 60°C or sodium chlorite at 80°C. In case of chlorite bleaching, the treatment should be followed by an antichlor.

The polyamide fibres are largely bleached with sodium chlorite. It gives better whiteness than that obtained by hydrogen peroxide or peracetic acid. It does not have any harmful effect on the fibre. The bleaching liquor may contain:

0.5–2.0 g/L	Sodium chlorite (80%)
0.5–1.0 g/L	Tetrasodium pyrophosphate
0.5–1 g/L	Wetting agent
1–2 g/L	Sodium nitrate

and sufficient formic acid to maintain pH between 3.8 and 4.2.

The bleaching is carried out 80–85°C for 30–60 min. After bleaching, the material is washed with hot and cold water followed by antichlor with 1–2 g/L sodium bisulphite at 20–55°C for 15 min. The material is finally washed with cold water.

100% polyester fabrics contain few impurities and have a naturally good white colour. Sodium chlorite has some bleaching effect on polyester – other bleaching agents are ineffective. It does not cause damage to the fibre and indeed, there is a slight increase in the degree of crystallisation. The bleaching may be carried out with 1–5 g/L sodium chlorite for about 1 h, best at 98–100°C and practically at 90–95°C, to minimise the evolution of intolerable chlorine dioxide.

Acrylics also possess good natural whiteness and for extremely good whiteness, bleaching may be carried out with sodium chlorite solution containing:

- 1.5 g/L sodium chlorite
- 1–2 g/L stabiliser (polyphosphates, formates, borax) to control release of chlorine dioxide
- 1–2 g/L sodium nitrate
- 2 g/L oxalic or formic acid to bring pH between 3.8 and 4.2.

Non-ionic detergent and fluorescent whiteners stable to chlorine dioxide may be incorporated in the bleaching bath for simultaneous scouring and optical whitening respectively.

The bleaching is carried out at 90°C for 2 h followed by an antichlor.

Peracetic acid has been put forward in recent years as a suitable bleaching agent for many fibres – nylon, viscose rayon, cellulose acetate and even cotton as a possible substitute of hydrogen peroxide. It is particularly recommended for bleaching nylon, which becomes yellowish during the heat-setting process. Degradation of nylon by peracetic acid is not significant and is not dependent on pH.

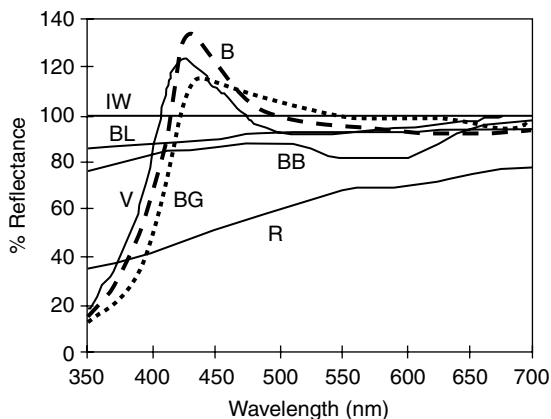
Bleaching may be carried out on nylon for about 2 h at 80°C using 3 g/L peracetic acid (36–40%), 0.2 g/L sodium pyrophosphate and wetting agent at pH between 6.0 and 7.5 with dilute caustic soda.

It is possible to bleach viscose and acetate fibres satisfactorily at pH 6.0–8.0; no damage by saponification will occur to the acetate fibres.

### 3.18 Improvement of whiteness

Natural fibres like cotton and wool absorb more light in the blue region of the visible spectrum than in the others owing to the presence of impurities, i.e. natural colouring matters. Consequently, they take on a yellowish or brownish cast. Whiteness of such substances can be improved in three ways:

1. Increasing blue reflectance of the substrate by destroying the colouring matter with strong reducing or oxidising agents in the process called bleaching. The function of bleaching is to remove blue-absorbing yellow contaminants.
2. Even the most thorough bleach cannot remove all traces of yellowish cast. Therefore, an additional whitening stage is essential. The age-old practice was to treat the bleached material with a very small amount of a blue or violet dye – an operation known as ‘bluing’ – to boost the visual impression of whiteness. The most widely used colourant for the purpose is a water-insoluble pigment available commercially in finely powdered form called Ultramarine Blue (C.I. pigment blue 29/770077)



3.5 Reflectance curves for raw and treated cotton materials.

or dispersed in liquid form. The pigment is bright blue to bluish green in colour. It is fast to acid and alkali, but unstable in lime. The treatment is generally conducted at room temperature for a very short period. This treatment was very popular for domestic washing of white goods. The present trend is, therefore, to use a water-soluble dye having no affinity for the substrate, for example, a blue or violet acid dye for cotton. The commonly used dye is Milling Violet 5B (C.I. Acid Violet 49/42640).

3. The third method is to use fluorescent brightening agents (FBAs), fluorescent whitening agents or optical whitening agents. FBAs are virtually colourless compounds which, when present on a material, have the ability to absorb mainly invisible ultraviolet light in the 300–400 nm range and emit violet to blue fluorescent light. The emitted fluorescent light is added to the light reflected by the treated material, by that producing an apparent increase of reflectance in the blue region. ‘Dazzling’ whiteness is perceived especially on a well-bleached material. Slight improvement in base whiteness enhances whiteness of FBA-treated material significantly. Figure 3.5 shows reflectance curves of unbleached raw cotton (R), bleached (BL), bleached and blued (BB) and differently tinted FBA-treated cotton materials – violet (V), blue (B) blue-green (BG). The curve for physically ideal white (IW) is also shown for comparison.

### 3.18.1 Fluorescent brightening agents

An FBA is a dyestuff, but in place of the chromophoric system which is a characteristic for dyes, it contains a fluorescing system and similar to a normal dye, has certain substituents which promote the affinity, depending on the type of fibre on which it is applied.

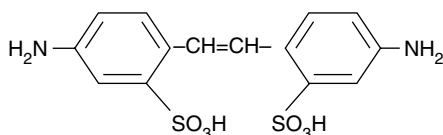


The FBAs can be classified into six groups (Sabale and Rane, 2009):

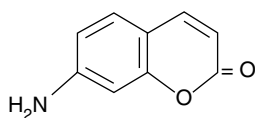
1. Triazine-stilbenes (di-, tetra- or hexa-sulphonated) and Biphenyl 1-stilbenes
2. Coumarins
3. Imidazolines
4. Diazoles
5. Triazoles
6. Benzoxazolines.

The chemical structures of these agents contain aliphatic carbon-carbon double bonds, which are responsible for substantivity and are sensitive to sunlight, oxidation, weathering, etc. The products suitable for cotton are more or less substantive and are derivatives of diaminostilbene disulphonic acid (Fig. 3.6). Tinopal BV (Geigy) was one of the early products, which achieved great success. It has good affinity for cellulosic fibres and has sufficient blue fluorescence to give commercially acceptable whites. Acid-stable, acid dye-type diaminostilbene whiteners are applicable on wool and polyamides. A great number of products are based on 7-aminocoumarin (Fig. 3.7). Aminocoumarins have been specially marketed for application to wool and nylon. These are water-soluble compounds, which are widely used on cellulose, polyamide and wool fibres. There are also interesting representatives among the products based on 3-phenylcoumarins (Fig. 3.8). Many of the currently used FBAs are derived from heterocyclic compounds, which contain nitrogen atoms.

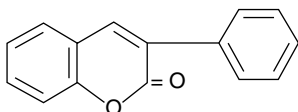
Polyester fibres are highly hydrophobic substances and only dispersions of insoluble fluorescent compounds can be used on them. They are mostly



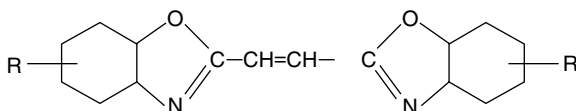
3.6 Diaminostilbene disulphonic acid.



3.7 7-Aminocoumarin.



3.8 3-Phenylcoumarins.



3.9 Bisbenzoxazole compounds.

applied along with finishing agents by pad-cure method. Bisbenzoxazole compounds (Fig. 3.9) and many other heterocyclic compounds are suitable, provided none of the substituent groups are sulphonic groups.

Most of the acrylic fibres have affinity for cationic FBAs. Figure 3.9 will be suitable provided the R and R' are amino or substituted amino groups. Basic naphtho-triazol stilbene, oxacyanines and pyrazoline derivatives are also being used (Trotman, 1968).

Cellulosic fibres generally require between 0.05 and 0.6% (o.w.m.) FBAs, when applied from long liquor by exhaustion methods. The most commonly used are Tinopal 2B, BV, ABR, Blankophor CE, BE, RA, BA, etc. Amongst the FBAs used for wool and silk are Tinopal WG, Uvitex WGS and Blankophor WT. They all contain sulphonic acid groups and behave towards protein fibres like acid dyes. Approximately 0.02–0.2% (o.w.m.) of FBAs is applied from an acid dyebath having pH between 3.0 and 5.0 by addition of organic acids. The treatment is carried out at 40°C for 20 min.

The disperse FBAs such as Tinopal PG, Tinopal ET and Uvitex ERN are available in paste form. They are applied from neutral liquors at high temperature of 70–80°C. The rate of exhaustion is slower and a treatment for 30–45 min at the specified temperature is necessary.

The optical whitening agent can also be applied successfully on polyester by pad-bake method. The fabric is run through a padding liquor containing 1–30 g/L optical whitening agent. It is then dried and cured at 120–160°C on a stenter machine. The fastness to washing and light of optical whitening agent on polyester are of high order.

Most of the acrylic fibres contain anionic groups conferring affinity for cations. The cationic FBAs are applied from liquors containing 3–5% formic acid to bring pH of 3.0–4.0. The treatment is carried out at a temperature of 95–100°C for 30–40 min. The exhaustion can be improved by treating at a temperature of 110°C in a pressurised vessel.

Good preparation of textile materials will reduce faults during dyeing, printing and finishing. Such an important component of textile wet processing demands more attention from the processors and researchers. Attention is focused on preparation steps only when a dyeing/printing fault is revealed. The classical methods of preparation have not been challenged or changed significantly after several decades except for the introduction of continuous preparatory processing as a substitute for batch processing. The preparatory processes are mostly run conventionally. Successful coloration and finishing require optimised preparation processes. Of course, optimisation is quite difficult due to wide batch-to-batch variation of the substrates.

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**Abstract:** This chapter briefly discusses the chemistry, properties and principles of applications of various textile dyes, namely, direct, reactive, disperse, acid, azoic, vat and sulphur.

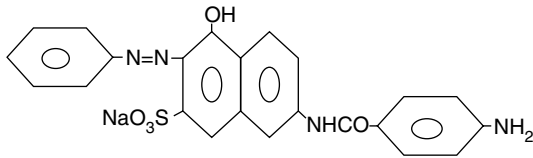
**Key words:** acid, azoic, chemistry, direct, disperse, properties, reactive, sulphur, vat.

## 4.1 Fundamental principles of direct dyeing

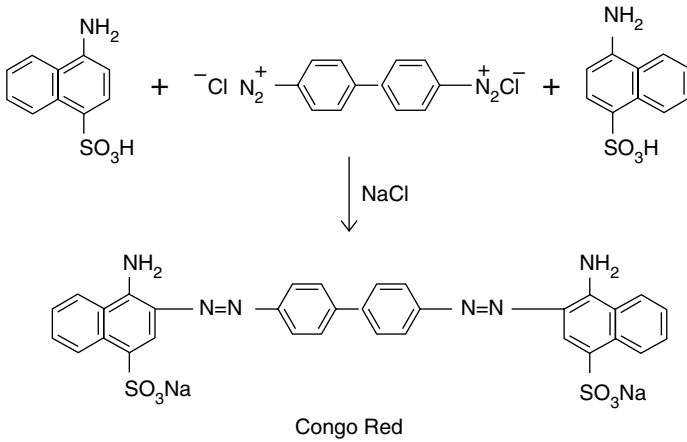
### 4.1.1 Chemistry of direct dyes

Congo Red, the first direct dye, was discovered in 1883 by Paul Bottinger, who was working as a dye chemist for the Friedrich Bayer Company in Ebersfeld, Germany (Garg and Nigam, 1981; Linke, 2006). Bottinger left his employer, patented the compound under his own name and then sold the patent to AGFA in 1885. Today a great number of direct dyes are known which give a wide range of colours and are popularly used for the dyeing of cellulosic textiles.

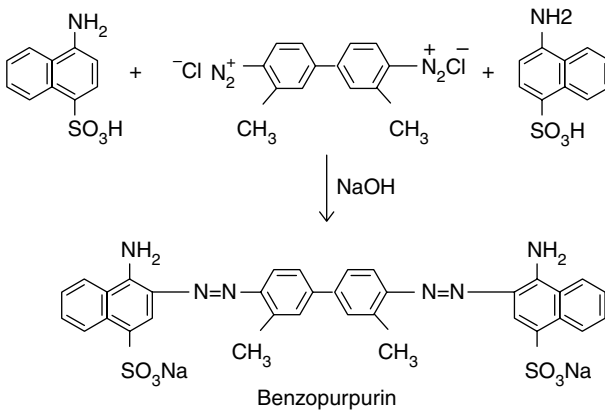
The chromophoric group of direct dyes includes azo, stilbene, oxazine and phthalocyanine, with some thiazole and copper complex azo dyes (Aspland, 1997). The majority of direct dyes belong to the azo class. Direct dyes are synthesised by coupling a coupler, containing a hydroxyl, amino or other groups with an aromatic diazotised base. Polyazo dyes are made either from a diamine such as benzidine, o-toluidine, or o-dianisidine or by diazotising an aromatic amine and coupling it with another aromatic amine. This amine may also then be diazotised and further coupled with other suitable compounds (Karmakar, 2007). An example of a monoazo direct dye is C.I. Direct Red 14 (Fig. 4.1). Congo Red is synthesised by coupling bis-diazotised benzidine with two molecules of naphthionic acid. The blue dye so obtained is converted into its red disodium salt during its salting out with sodium chloride (Fig. 4.2). Similarly benzopurpurin is prepared by coupling bis-diazotised o-toluidine with two molecules of naphthionic acid (Fig. 4.3).



4.1 C.I. Direct Red 14.

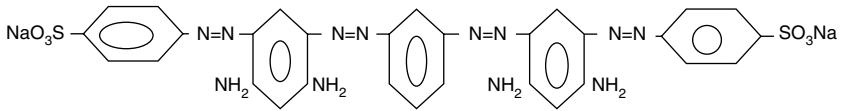


4.2 Congo Red dye.

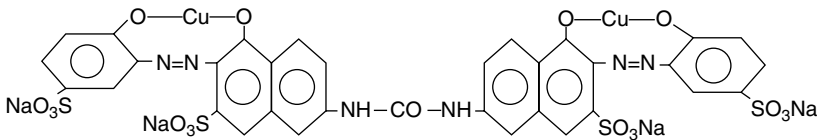


4.3 Benzopurpurin.

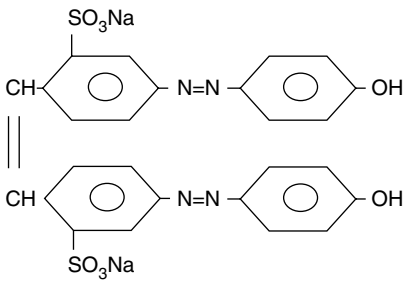
The examples of polyazo (C.I. Direct Brown 44), metal complex (C.I. Direct Red 83), stilbene (C.I. Direct Yellow 19), phthalocyanine (C.I. Direct Blue 86) and thiazole (C.I. Direct Yellow 8) based direct dyes are shown in Figs 4.4–4.8.



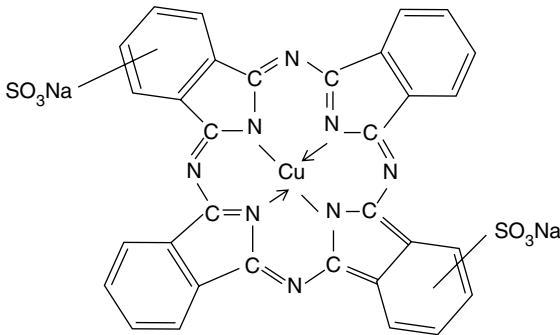
4.4 C.I. Direct Brown 44.



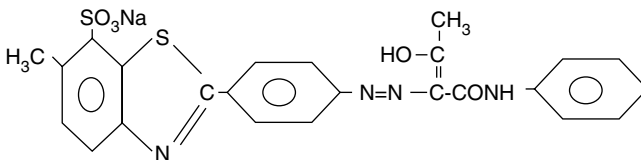
4.5 C.I. Direct Red 83.



4.6 C.I. Direct Yellow 19.



4.7 C.I. Direct Blue 86.



4.8 C.I. Direct Yellow 8.



The German Consumer Goods Ordinance (1994) banning the use of certain azo dyes, which came into effect in 1996, has severely restricted the use of direct dyes. Some of the bisazo dyes derived from benzidine have a carcinogenic effect, including Congo Red. Congo Red has therefore been withdrawn globally from the manufacturing range of many dyestuff manufacturers.

#### 4.1.2 Classification of direct dyes

Direct dyes have high substantivity and are influenced by various dyeing parameters such as temperature, concentration of electrolyte, etc. Lemin *et al.* (1946) studied the effect of various parameters on the kinetics of dyeing with a number of direct dyes. On the basis of their observations they suggested that the dyes should be classified into three groups. They are as follows.

##### *Group A*

These dyes are also known as self-levelling dyes. Dyes belonging to this group migrate well and therefore have high levelling power. When dyeing with these dyes, the dyeing may be uneven initially but continued dyeing levels out the shade. Mostly, they are monoazo or disazo dyes with at least two solubilising groups. Dyes belonging to this group dye uniformly even when the electrolyte is added at the beginning of the dyeing operation. They may require relatively large amounts of electrolyte to exhaust well.

The maximum exhaustion of these dyes takes place between the temperature range 60° and 80°C. Some examples of this class of dyes are Paramine Fast Red 8BL, Sirius Light Yellow R and Direct Blue 3RL.

##### *Group B*

The migration property of these dyes is poor and therefore they are not self-levelling. Their exhaustion has to be brought about by controlled addition of an electrolyte. These classes of dyes are called salt-controllable dyes. The addition of the electrolyte should be made in instalments to achieve uniform dye absorption. If these dyes are not taken up by the fibre uniformly in the initial stages of dyeing, it is very difficult to even out the shade later. They are mostly disazo dyes with three to four solubilising groups. Examples of these dyes are Azonine Scarlet 8B and Chloramine Fast Red F.

##### *Group C*

These dyes are called temperature-controllable dyes although they should be called salt and temperature-controllable dyes since their rate of exhaustion

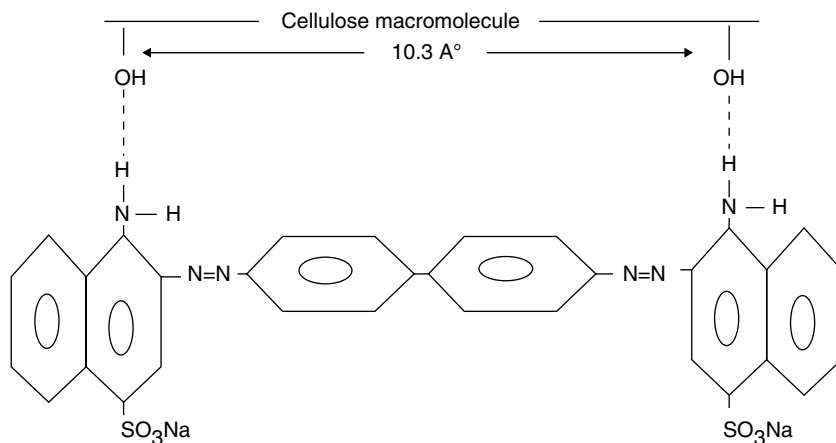
depends highly on the addition of salt and the rate of rise of temperature. These dyes require less amounts of salt than class A and B dyes. Extreme care should be taken in making the electrolyte addition for this class of dyes; similarly to class B dyes, addition of the electrolyte should be conducted in instalments. Carbide Black E belongs to group C class of direct dyes.

The dyes from the same group should be selected for compound shades. However, selected dyes from groups A and B, and groups B and C may be dyed together in the same bath in exhaust dyeing (Horrocks and Anand, 2000).

#### 4.1.3 Properties of direct dyes

The direct dyes in the Colour Index system refer to various planar, highly conjugated, molecular structures containing one or more sodium salts of sulphonic acid, which impart solubility to the dyes. Their planar structure and length enable them to lie alongside cellulose fibres and maximise the van der Waals, dipole and hydrogen bonds (Fig. 4.9). The interactions between the hydroxy groups of cellulose and the delocalised  $\pi$  electron system of the dye molecule as a whole make a major contribution to substantivity of the dyes towards the fibre.

Solubility decreases with the increase in molecular weight of the dyes. Prolonged storage or exposure to acidic fumes in the atmosphere converts the sodium sulphonate ( $\text{SO}_3\text{Na}$ ) group to the  $\text{SO}_3\text{H}$  group, which results in a loss of solubility of the dyes. During dissolution of the dye, therefore, addition of sodium carbonate is required to obtain the sodium salt of the sulphonic acid group.

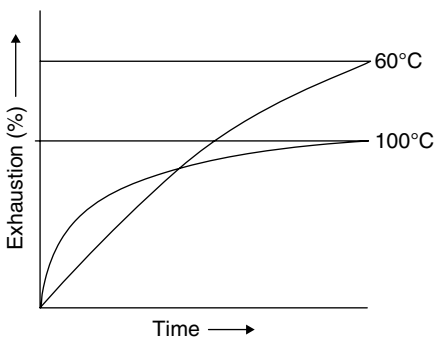


4.9 Chemical bonding between cellulose and direct dye.

Cellulosic fibres develop a negative surface charge (zeta potential) when in contact with an aqueous dyebath (Chattopadhyay, 2001). Direct dyes being anionic in nature experience a repulsion force between the dye and the fibre in the dyebath, which lowers the exhaustion of the dye. The addition of an electrolyte helps in neutralising this negative zeta potential and hence facilitates the approach of the direct dyes towards the fibre.

The wash-fastness properties of direct dyes are generally poor-to-moderate whereas light-fastness is generally found to be poor-to-very good. However, nowadays environmentally friendly direct dyes with excellent washing- and light-fastness are available on the market. Some of the azo direct dyes are stable at high temperature and can be used along with disperse dyes for the dyeing of polyester/cotton blended materials. Pre-treatment of cotton with cationic agents such as mono- and bis-reactive 2,3 epoxypropyl derivatives was found to enhance the direct dye uptake greatly (Sharif *et al.*, 2008). Clariant has produced a metal-free, very light-fast, Indosol SF series of dyes. The formaldehyde-free dye fixing agent Indosol E50 liquid has been introduced, which improves the wet-fastness properties of dyeings on cellulosic fibres with Indosol direct dyes.

The major factors affecting the absorption of direct dyes by cellulosic fibres include the length of time of dyeing, temperature of dyeing, liquor ratio, electrolyte concentration, solubility and aggregation properties of the dyes used. When other factors remain constant, an increase in the temperature will cause a decrease in the equilibrium exhaustion but an increase in the rate of dye absorption (Fig. 4.10). At the commencement of dyeing the free energy of the dyes in solution is greater than that of the dyes in the fibre phase. The difference in free energy is the driving force to transfer the dye molecules to the fibre until a state of equilibrium is reached. The attainment of equilibrium involves a decrease in the total free energy of the system. Heat is released during the operation, which makes the dyeing process exothermic in nature. Therefore, an increase in temperature reduces the equilibrium dye



4.10 Effect of dyeing temperature on direct-dye uptake.

uptake. The phenomenon may also be explained by the loss in the affinity of the dyes with the rise in temperature. For a fixed dyeing time there is an optimum temperature at which maximum dye exhaustion takes place.

Dyebath exhaustion is inversely affected by an increase in liquor ratio; hence the colour depth will vary largely among various methods of dyeing with varying liquor ratios. To have reproducible results, the liquor ratio in subsequent batches should be maintained. As discussed earlier, the addition of an electrolyte to the dye liquor tends to enhance the exhaustion of anionic dyes such as direct dyes. However, the effect varies considerably with different dyestuffs.

The effectiveness of electrolytes in enhancing exhaustion varies with the number of sulphonic acid groups present in the dye molecules. The greater the number of sulphonic acid groups in a dye, the higher the repulsion factor will be and consequently the greater the dependence on the electrolyte concentration.

#### 4.1.4 Principles of direct dye application

The dye powder is dissolved by pasting it with cold water and a small amount of soda ash. Anionic or non-ionic wetting agents may also be used in pasting the dye. Boiling water is then poured over the paste with constant stirring to achieve dissolution of the dye powder. The solution is then added to the dyebath side tank via a strainer. Soft water is preferred but it is not essential. For hard water sensitive dyes, sequestering agents may be used.

For the dyes in the group A category, the dyebath is set at 40–50°C. Desized, scoured and optionally bleached cellulosic material is dyed for about 10 min and 5–20% electrolyte on the weight of the material (or approximately 10–15 g/L) is added depending on the depth of shade required. The temperature is slowly raised to boil over a period of 30–40 min and dyeing is continued at this temperature for 45–60 min. Improved dye exhaustion may be achieved by running the material for some time in the cooling bath at around 80°C. Addition of a further 2% electrolyte in the cooling bath can enhance the dye exhaustion. The dyebath is drained and the material is thoroughly washed with cold and hot water. Soaping is normally avoided but with the recent introduction of high wet-fastness dyes, soaping can be carried out without any danger of major colour loss.

The method used for the group B dyes is almost same but as these are salt-controllable dyes, extreme care has to be taken in electrolyte addition. The addition should be made in instalments, with a gradual rise in the amounts added. The most preferred method will be addition through drip feeding. Levelling agents are also recommended to reduce the electrolyte sensitivity of the dyes (Roy Choudhury, 2006).

Group C dyes are dyed with extreme care in the electrolyte addition and the temperature rise. Here, similar to the group B dyes, the electrolyte should be added in instalments, initially in small amounts and as dyeing proceeds the quantity may be increased. The rate of temperature rise should be carefully controlled especially near the temperature of maximum exhaustion of the dye. Either common salt (NaCl) or Glaubers' salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) may be used as the electrolyte. Common salt is less expensive than Glaubers' salt but Glaubers' salt is preferred over common salt as the latter may corrode stainless steel dyeing equipment at high temperature.

Fastness properties of the dyed materials may be improved by various well known after-treatments such as treatment with either copper or chromium salt and treatment with cationic dye fixing agents.

Unless after-treated, the stripping of direct dyes from dyed fabric is relatively easy, especially in the case of class A dyes. The dyes may be removed by boiling with a soap solution, or the dyes may be stripped by the reduction and solubilisation of the dyes using sodium hydrosulphite in the presence of caustic soda or by bleaching with a suitable bleaching agent.

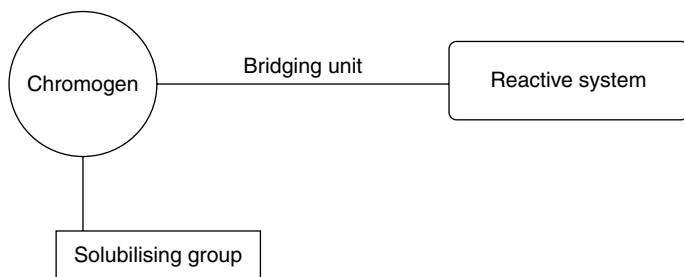
## 4.2 Fundamental principles of reactive dyeing

### 4.2.1 Chemistry of reactive dyes

Reactive dyes have been very popular for the dyeing and printing of cellulosic fibre for many years. The fibre-reactive dyes were first introduced as the Procion dyes of ICI in 1956 for the production of fast brilliant colours on cellulosic materials by continuous dyeing methods (Chattopadhyay and Chaudhary Ritu, 1997; Christie, 2001). Reactive dyes immediately proved attractive to dyers due to the bright colours and the excellent fastness properties of this new dye class. This immediate interest was further increased when batch dyeing methods for these dyes were developed. They are water-soluble anionic dyes and various physical forms of these dyes are available such as pourable granules, finished powders and highly concentrated aqueous solutions, whereas in the past dyes were mainly marketed as powders. There are also commercially available fibre-reactive dyes for protein and polyamide fibres. The general formula for the reactive dyes may be schematically represented as shown in Fig. 4.11.

Reactive dyes consist of four parts:

1. The chromogen or the chromophoric part, which contributes colour to the dye.
2. The reactive system, which enables the dye to react with the substrate. This part can also react with water molecules present in the dyebath, a



4.11 Schematic structure of reactive dye.

phenomenon called hydrolysis of the reactive dyes which is not a desirable reaction during dyeing.

3. A bridging unit that joins the reactive system to the chromophoric part.
4. The solubilising group(s) attached to the chromophoric grouping confers water solubility to the dye.

In a few cases the reactive part remains attached directly to the dye. Substituent groups and the nature of the bridging unit affect the reactivity and dyeing characteristics of dyes.

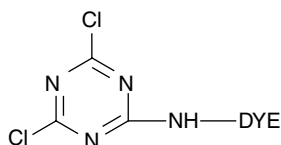
The majority of reactive dyes are chemically of the azo class, although anthraquinone-based reactive dyes are also available.

#### 4.2.2 Classification of reactive dyes

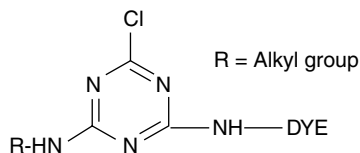
Depending on the type of reaction, the reactive dyes are broadly divided into two categories:

1. Dyes reacting through the nucleophilic substitution reaction
2. Dyes reacting through the nucleophilic addition reaction.

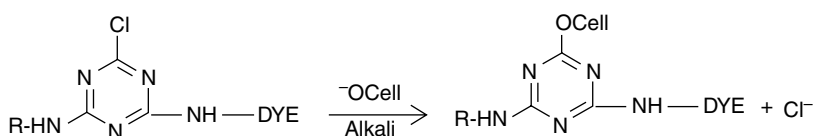
Triazine-based reactive groups react through the nucleophilic substitution reaction. They are mostly chlorotriazines of either the dichloro or monochloro type. The reactivity of dichlorotriazine-based dyes is higher than the monochloro dyes so they require a lower temperature and a milder alkali for their application when compared to the monochloro dyes. These dyes are known as cold brand reactive dyes. The trade names of some cold brand dyes are Reactofix M (Jay Synth), Procion M (Atul) and Procion MX (Zeneca). The general chemical structure of these dyes is shown in Fig. 4.12.



4.12 General structure of cold brand reactive dye.



4.13 General structure of hot brand reactive dye.



4.14 Reaction of cotton cellulose with reactive dye.

Monochlorotriazine dyes require a higher temperature and a stronger alkali application than the dichlorotriazine-based dyes. Monochlorotriazine dyes are available on the market in different trade names such as Procion H (Atul), Reactofix H (Jay Synth), Amaryl X (Amar Dye Chem), etc. The letter 'M' and 'H' in the trade names of dichlorotriazine and monochlorotriazine dyes respectively stand for cold brand dyes and hot brand dyes. The general structure of monochlorotriazine-based hot brand reactive dyes is presented in Fig. 4.13.

The reaction of triazine dyes with cellulose is shown in Fig. 4.14. The chlorine of the triazine ring is replaced by OCellulose. Thus the dyes form a covalent bond with the fibre, which accounts for the high wash-fastness of reactive dyes. The reactive dyes can react with water molecules as well. The reaction of the dyes with water is called hydrolysis. The hydrolysed dyes lose their power to react with the fibre. These dyes remain loosely held on the fibre and if not properly removed through thorough soaping, they deteriorate the wash-fastness of the dyes. The nature of the electrolyte used plays an important role in the absorption of the hydrolysed dye. Shrivastava (1979) studied the effect of various electrolytes on the absorption of the hydrolysed dye on cotton and found that their relative efficiencies were in the order: ammonium chloride > ammonium sulphate > sodium chloride > lithium chloride ~ magnesium chloride. Ciba Geigy developed Cibacron F dyes where fluorine is used in place of chlorine as the leaving group.

The majority of the dyes that react through nucleophilic addition reactions are based on vinyl sulphone. The general formula of these dyes may be written as  $D\text{SO}_2\text{CH}=\text{CH}_2$ . They are marketed in the soluble form that is  $\beta$ -hydroxy ethylene sulphone derivatives  $D\text{SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na}$ , where D stands for dye chromophore. Colour Chem produce this dye under the trade name Remazol. Dyes having an acrylamido-based reactive system were developed by BASF (Primazine dyes) and Ciba Geigy (Lanasyn/Lanasol dyes). The general structure of these dyes is  $D-\text{NHCO}-\text{CHX}=\text{CH}_2$ . The carbonyl group is a less powerful electron-withdrawing group so the reactivity of these dyes is less compared with vinyl sulphone dyes. Dyes containing heterobifunctional groups like Sumifix dyes (Sumitomo Chemical Co.), which contain both chlorotriazine and vinyl sulphone reactive groups are also very popular. The bond between vinyl sulphone and cellulose is very strong and is stable to acid hydrolysis. Also the substantivity of hydrolysed dyes is very poor and so unfixed hydrolysed dyes can be washed off easily. The advantage of the chlorotriazine group is that it increases the substantivity of the dye and thus improves the degree of exhaustion and fixation of dye.

#### 4.2.3 Properties of reactive dyes

In general, textile materials coloured with reactive dyes have very good light-fastness, the light-fastness rating being about six. The very stable electronic arrangement of these dyes provides good resistance to the degrading effect of sunlight. There are, however, some reactive dyes with only fair light-fastness. Reactive dyes with azo chromophore show lower light-fastness. Metal complex type azo reactive dyes have higher light-fastness. Textile materials coloured with reactive dyes have good wash-fastness; their wash-fastness rating is about four to five. This is attributed to the very stable covalent bond that exists between the dye molecule and the cellulosic fibre. Perspiration and atmospheric pollution, which are both acidic in nature, may affect textile materials that are dyed or printed with reactive dyes and result in some fading. It is found that textiles dyed with bactericidal monochlorotriazine reactive dyes containing hexachlorophene possess a wide spectrum of bactericidal action (Kalontarov and Kalandarov, 1993). This effect is reported to depend on the dye functionality based on phenol OH-groups. With monofunctional dyes the effect is three to eight times larger than observed with dyes containing disubstituted hexachlorophene residue.

There are various reports published in the literature on the effect of cross-linking with reactive dyes on the fibrillation of lyocell fibres (Bates *et al.*, 2008; Goswami *et al.*, 2007; Phillips *et al.*, 2008).



#### 4.2.4 Principles of reactive dye application

The methods by which reactive dyes can be applied are as follows:

- (i) Exhaust method (on jigger/winch)
- (ii) Padding method.

The exhaust technique is the most common method for application of reactive dyes as it is resistant to small changes of system variables. It comprises two steps: exhaustion and fixation. During exhaustion the dyes are exhausted from the dyebath and come into the fibre phase. High electrolyte concentration is required to have adequate exhaustion of the dye. Various techniques of cationisation of cotton for saltless dyeing are reviewed in detail by Chattopadhyay (2001). One method of salt-free reactive dyeing of cotton using 1,2-dichloroethane followed by amination with a suitable amino compound has been reported by Chattopadhyay *et al.* (2007).

The fixation of the dye takes place in the presence of an alkali. After the addition of the alkali, the migration of the dyes ceases and they start reacting either with the fibre or with the water molecules. After the fixation, the treated material is thoroughly rinsed to wash off the loose unfixated dyes.

The padding method has several advantages over the exhaust method (Janakiraman and Narasingha, 1977) such as:

- lower consumption of steam, electricity, dyes and chemicals
- higher productivity
- high degree of fastness
- improved appearance.

Various sequences possible in this technique are as follows:

- (i) Pad-batch-wash
- (ii) Pad-dry-pad (alkali)-batch-wash
- (iii) Pad-dry-jigger develop-wash
- (iv) Pad-jigger develop (wet-on-wet)-wash
- (v) Pad-dry-pad (alkali)-steam-wash
- (vi) Pad-dry-cure-wash
- (vii) Pad-dry-hot alkali pad-wash.

The detailed methods of these techniques are summarised by Chattopadhyay and Chaudhary Ritu (1997).

## 4.3 Fundamental principles of disperse dyeing

### 4.3.1 Chemistry of disperse dyes

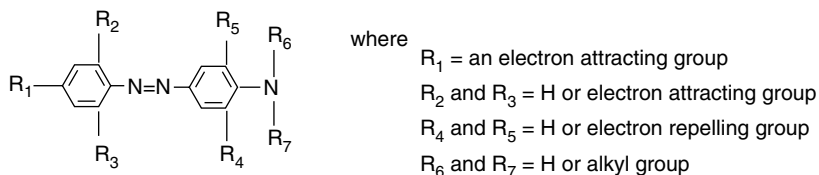
The history of development of disperse dyes is intimately associated with the synthesis of cellulose acetate fibres which were introduced into the market in the early 1920s. Monoazo is the largest class (50%) of disperse dyes. Most of the yellow, orange, red, brown and black dyes belong to this group. A generalised structure of disperse dye is shown in Fig. 4.15. Monoazo disperse dyes are easy to manufacture and are available at a relatively cheap cost but many of them have poor sublimation fastness.

About 10% of the disperse dyes are based on the disazo compound. These dyes have excellent fastness properties and are especially suitable for application by the thermofixation process. They have good light-fastness and sometimes more polar groups are introduced to increase the sublimation fastness. They are mainly yellows and oranges.

Anthraquinone-based disperse dyes constitute about 25% of the total disperse dyes available in the market. Therefore monoazo, disazo and anthraquinone constitute about 85% of the total disperse dyes. The remaining 15% of the dyes belongs to styryl (3%), methine (3%), arylbenzimidazole (3%), quinonaphthalone (3%), nitro (1%), aminonaphthlimide (1%) and naphtho-quinoneimine (1%). The anthraquinone-based disperse dyes are difficult to synthesise and are therefore costlier than azo-based dyes but they are relatively brighter. They are more stable at high temperature compared with azo- or styryl-based dyes. Styryl dyes are useful for the production of bright greenish-yellow colours with good fastness to light. Some of the anthraquinone-based dyes are poor in gas fume fading and sublimation fastness. The introduction of polar groups or an increase in molecular size improves the fastness towards sublimation. Some of the yellow and orange dyes are based on a nitrodiphenylamine structure. They are cheaper dyes and have very good fastness to light.

### 4.3.2 Properties of disperse dyes

Disperse dyes on synthetic materials have a moderate-to-good wash-fastness. The better wash-fastness may be attributed to the insolubility of the



4.15 General structure of monoazo disperse dye.

dyes and to the hydrophobic nature of the synthetic fibres. The wash-fastness ratings range between three and five.

The light-fastness rating is found to lie between four and five. The fair-to-good light-fastness rating may be attributed in part to the non-ionic nature of the dye molecules, which will not readily attract water or other polar molecules that may have an accelerating effect on light fading. The ultra-violet (UV) component of sunlight may cause some colour fading due to prolonged exposure of the dyed materials in sunlight.

As discussed earlier, some of the disperse dyes with the anthraquinone structure, especially blue and violet dyes, fade in the presence of nitrous oxide from polluted air. Nitrous oxide fading can be minimised by treating the dyed material with a chemical based on an azoic thiophene–benzene complex (Gohl and Vilensky, 1987). The improved resistance to gas fading occurs because the nitrous oxide will react with this complex in preference to the disperse dye molecules.

### 4.3.3 Principles of disperse dye application

Polyester fibres are extremely crystalline, hydrophobic in nature and have a high glass transition temperature ( $T_g$ ). Hence the fibre requires a high temperature around 130°C for its dyeing. To obtain such a high temperature high pressure (HTHP) is required. This method of dyeing is therefore called the HTHP dyeing method. For dyeing using the HTHP method special equipment is required which can withstand such conditions. Alternatively, the fibre can be dyed in a boiling dyebath at atmospheric pressure in the presence of some plasticisers which are capable of reducing the  $T_g$  of the fibre. These agents are known as carriers; the method of dyeing is therefore called the carrier dyeing method. There are various explanations available for the mechanism of carrier action. Amongst them the most modern explanation is the reduction of the  $T_g$ . Many scientists claim that the carriers work by swelling the fibre but there are many carriers available that cannot swell the fibre and still they are efficient in their carrier action. As disperse dyes are insoluble or only slightly soluble in water, they are applied from an aqueous dispersion in the presence of a dispersing agent. Disperse dyes require slight acidity for their exhaustion into the fibre. The acidity is achieved by adding acetic acid to achieve a pH of 4.0–4.5. The insolubility of the disperse dyes enables them to leave the dye liquor as they are more substantive to the hydrophobic polyester fibre. Heating the dye liquor will accelerate the strike rate and the diffusion of the dyes inside the fibre structure. Once within the fibre polymer system, the dye molecules are held by hydrogen bonds and van der Waals forces.

The desirable characteristics of a carrier are (a) ready availability, (b) low price, (c) non-toxic and lacking an unpleasant odour, (d) efficiency in terms

of the amount required to have a satisfactory effect, (e) easy removal from the dyed material, (f) non-volatile, (g) inert to the dye and fibre, (h) biodegradable and (i) compatible with other dyebath auxiliaries. There are many organic compounds which act as carriers but only a few exhibit sufficiently attractive properties to be used in commercial dyeing. Carrier dyeing is relatively expensive and most of the carriers are not environmentally friendly. Many of them have an unpleasant odour and affect the light-fastness of the dyed materials if not removed efficiently after the dyeing is over. Because of these limitations the HTHP process is preferred. Besides these two batch methods there is one process for continuous dyeing of polyester available which is known as thermofixation or the thermosol method. This was developed by Dupont in 1949. The process comprises impregnating polyester fabric with an aqueous dispersion of disperse dye and drying and exposing the dried fabric to heat at a temperature of 180–230°C for a few seconds to effect the fixation and the uniform distribution of dyes within the fibre Moorhouse (1996).

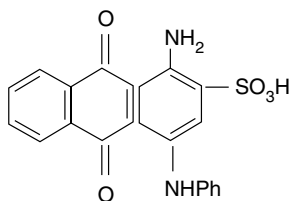
## 4.4 Fundamental principles of acid dyeing

### 4.4.1 Chemistry of acid dyes

Acid dyes are typically used to dye natural protein (wool and silk), synthetic polyamide (nylon) and to a small extent acrylics and blends of these fibres. They are so called because they are applied to these fibres from dyebath in acidic or neutral conditions. The generic term ‘acid dyes’ includes several individual dye classes. As per the Colour Index definition, metal complex dyes are also included in the category of acid dyes. Chrome dyes are also considered as acid dyes. Here we will restrict our discussion to true acid dyes only.

Most of the commercially available acid dyes are azo, anthraquinone or triphenyl methane-based. Although there are other acid dyes like azine, xanthane, nitro, indigoid, quinoline and carbolan dyes, these dyes are of limited commercial value. The most popular chromophore in acid dyes is the azo group. Following the discovery of the diazo reaction by Griess in 1858, both monoazo and bisazo dyes were produced. The first azo acid dye was formed by diazotising sulphanilic acid and coupling with  $\beta$ -naphthol.

Molecular weights of acid dyes range from 200 to 900. Most have one or two  $-\text{SO}_3\text{Na}$  groups which are water-soluble and capable of bonding with fibres having cationic sites. They give a wide range of bright colours on textiles, especially when monoazo and anthraquinone structures are used. Some of the anthraquinone greens and violets are more brilliant than azo dyes. An example of anthraquinone-based acid dye is shown in Fig. 4.16. Acid dyes based on the triphenylmethane structure and its heterocyclic forms are not very popular though they are known for their brilliancy.



4.16 Solway Ultra Blue B dye.

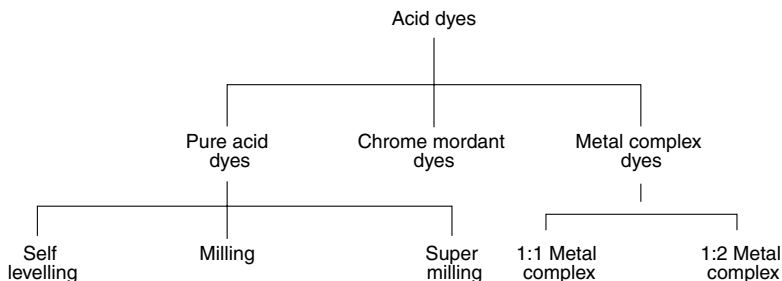
Carbolan dyes have a high fastness to milling treatment and washing. Azine dyes get reduced by the action of a reducing agent but their reduced form is soon oxidised by air.

#### 4.4.2 Classification of acid dyes

Acid dyes may be broadly classified as shown in Fig. 4.17. In use, acid dyes are classified by their dyeing behaviour and wet-fastness properties, rather than chemical classification (Bone *et al.*, 1988). The acid dyes are arbitrarily classified as self-levelling dyes, milling dyes and super milling dyes. The dyes which are to some extent fast to the milling treatment of wool are called milling acid dyes and the dyes which have very good fastness to milling are known as super milling dyes. The properties of these acid dyes are described in Table 4.1. Between self-levelling and milling acid dyes, another category called fast acid, half-milling or perspiration-fast acid dyes is also suggested in the literature (Duffield, 1992). The shade range available in this class is not as extensive as that of the self-levelling or milling dyes but it still covers a reasonably wide range. These dyes are recommended to be used for dark shades where conventional self-levelling dyes would have inadequate wash-fastness.

In another method of classification, acid dyes are classified into broad classes as molecularly split acid dyes and aggregated acid dyes. Self-levelling dyes are molecularly split acid dyes as they remain in molecularly split form in solution whereas milling and super milling dyes form aggregates when they are dissolved in water.

The smaller size and lesser affinity of self-levelling dyes allow them to migrate from one position to the other very easily and this gives a uniform dye application. On the other hand, the dyes can bleed during washing for the same reasons. A highly acidic condition is required to achieve proper exhaustion of these poor affinity dyes on the fibre. Super milling dyes are another extreme case; they have high molecular weight and very high affinity to protein fibres. The levelling properties of these dyes are therefore not good but they are fast to the washing treatments. For application of these



4.17 Classification of acid dyes.

Table 4.1 Properties of acid dyes

Property	Self-levelling acid dye	Milling acid dye	Super milling acid dye
Molecular size	Very small	Relatively bigger	Biggest
Affinity	Less	High	Very high
Migration property	Excellent	Poor	Very poor
Levelling	Excellent	Moderate	Poor
Wash-fastness	Poor	Good	Very good
Dyebath pH required	2–4	4–6	6–7
pH adjusting agent	Sulphuric/formic acid	Acetic acid	Acid liberating salts
Water solubility	High	Low	Low
Light-fastness	Very good	Good	Good
Behaviour in solution	Molecularly split	Aggregates	Aggregates

dyes a neutral pH condition is required. Milling acid dyes have properties in between these two extremes. Other types of acid dyes which are not included in this chapter are chrome mordant dyes and metal complex dyes.

#### 4.4.3 Properties of acid dyes

The electron arrangement in the chromophores of the acid molecules is such that they can resist the degrading effects of the UV radiation of the sun. The light-fastness rating of acid dyes is about four to five. The azo dyes generally show medium to good light-fastness properties, particularly in yellow, orange, red, brown and black shades. Azo violets, blues and greens have generally good light-fastness but they produce a duller shade compared with triphenylmethane dyes. The wash-fastness and other properties of the self-levelling, milling and super milling dyes are compared in Table 4.1. Dong *et al.* (2008) studied the decolouration behaviour of C.I. Acid Black

234 in water by the photocatalysis of  $\text{Fe}^{3+}$ -oxalate complexes/hydrogen peroxide system under different weather conditions in the presence of sodium chloride or sodium sulphate. They found that the presence of inorganic salt retards the photo-decolouration. Sodium chloride was found to exhibit a much stronger reduction effect on photocatalytic decoloration.

#### 4.4.4 Principles of acid dye application

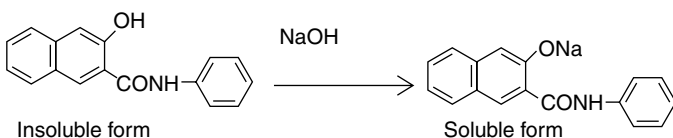
The application of acid dyes to protein or polyamide fibres results in an ionic linkage between the dye molecule and the fibre polymer. Wool or polyamide may be represented as  $\text{H}_2\text{N}$ -Polymer-COOH or simply Polymer-NH<sub>2</sub>. The amino groups present in the acid get protonated, forming Polymer-NH<sub>3</sub><sup>+</sup>. There are a large number of amino groups in wool fibre. There are approximately twenty times as many amino groups in wool as in nylon and five times as many amino groups in wool as in silk. The acid dye anions in solution experience a strong attraction towards the fibre because of the opposite nature of their charge. The application of acid dyes to protein or polyamide fibre thus results in ionic bonds or salt links between the dye molecules and the polymer. In addition to ionic links, when protein and polyamide fibres are dyed with acid dyes, hydrogen bonds as well as van der Waals forces will be formed between the dye molecule and the fibre polymer system. However, the ionic links between the acid dye molecules and the fibre polymer system play a greater role in the dye being retained by the fibre than the hydrogen bonds and van der Waals forces.

Electrolytes are used as retarding agents when dyeing self-levelling acid dyes (Kumazawa *et al.*, 1984), but electrolytes act as an exhausting agent in the case of milling and super milling types of acid dyes on wool.

## 4.5 Fundamental principles of azoic dyeing

### 4.5.1 Chemistry of azoic dyeing

The naphthols are insoluble in water. They are phenols, soluble in alkaline solution and substantive to cotton, particularly in the presence of salt. In the presence of a strong alkali they are converted to the corresponding naphtholate ions and are water-soluble (Fig. 4.18). The naphtholate ions are



4.18 Conversion of naphthol to naphtholate (dissolution of naphthol).

always coplanar and preferably have elongated molecular structures. These relatively small molecules are of low to moderate substantivity for cotton. The naphthols may be classified into four groups depending on their affinity for cotton (Shenai, 1993):

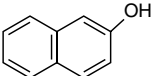
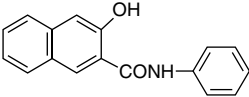
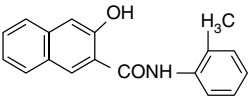
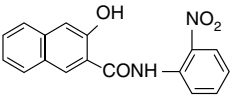
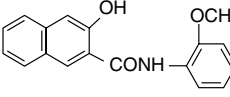
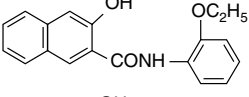
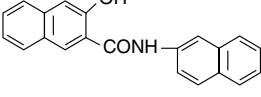
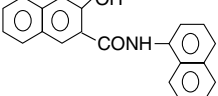
- (a) Low substantivity naphthols: Naphthol AS, Naphthol ASD, Naphthol AS-OL, Naphthol AS-IRG, Naphthol AS-PH, etc.
- (b) Medium substantivity naphthols: Naphthol AS-BG, Naphthol AS-LT, Naphthol AS-RL, etc.
- (c) High substantivity naphthols: Naphthol AS-BS, Naphthol AS-SW, Naphthol AS-BI, Naphthol AS-BO, etc.
- (d) Very high substantivity naphthols: Naphthol AS-BT, Naphthol AS-S, Naphthol AS-BT, Naphthol AS-BR, etc.

In general, the higher the substantivity the better the rubbing-fastness since less azo pigment forms on the fibre surfaces. Addition of salt promotes better exhaustion of the bath, more being needed for naphthols of lower substantivity. For the dissolution of naphthols usually a caustic soda solution of 72°TW, i.e. 38°Be, is used. The first azoic coupling component (ACC), which was employed in the commercial synthesis of azoic colour, was the 2-hydroxy-naphthalene, i.e. Beta-naphthol. The same was later replaced by more substantive arylamides of 2-hydroxy-3-naphthoic acid discovered in 1911 in Germany. This product is known today as Naphthol AS. With different substitutions on the basic structure, several other substantive naphthols were subsequently developed in the following years which were named as members of the Naphthol AS series (Table 4.2).

For *in situ* synthesis of azoic pigment on the textile material, the naphtholated material has to be developed in a bath containing a suitably prepared second component, usually referred to as a fast base. These are available as free amine base or as amine salts such as hydrochloride. Many of the amines used are simple substituted aniline derivatives. Some of these components are free bases ( $R-NH_2$ ), while others are hydrochlorides of the bases ( $R-NH_2.HCl$ ) and a few of them are hydrogen sulphates. The so-called fast colour bases require diazotisation for coupling with the naphthol. This usually involves a reaction of the primary aromatic amine in acidic solution or dispersion with sodium nitrite, at or below room temperature. Diazotisation of a primary aromatic amine is often difficult and solutions of diazonium ions are inherently unstable. They undergo decomposition even at low temperature and particularly on exposure to light. Storing prepared diazonium ion solutions is not usually possible. Table 4.3 shows some examples of the colour developed by various combinations of naphthols and fast bases. The first step in selecting the most suitable naphthol (coupling component) and



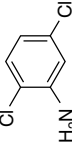
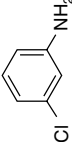
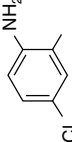
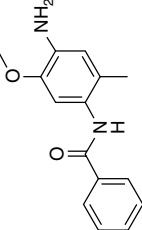
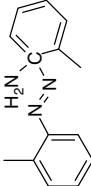
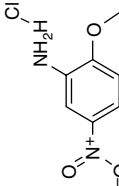
Table 4.2 Example of some naphthols (ACC)

Naphthol	Substantivity	Structure	C.I. constn. no	ACC
$\beta$ -Naphthol	–		–	–
Naphthol AS	Low		37505	2
Naphthol ASD	Low		37520	18
Naphthol AS-BG	Medium		–	19
Naphthol AS-OL	Low		37530	20
Naphthol AS-PH	Low		37558	14
Naphthol AS-SW	Higher		37565	7
Naphthol AS-BO	Higher		37560	4

fast base (diazo component) for a particular purpose is to decide which of the available naphthols, after dissolution, give anions with suitable substantivity for application by the desired method. The second step is to decide which of these naphthols can be used in conjunction with the available diazo components to produce the colour closest to the desired shade and depth (Aspland, 1997).

As discussed earlier, the naphthols are not soluble in water but their sodium salts (naphtholates) are water-soluble. The first step for the production of azoic colour on textile materials is, therefore, the dissolution of

Table 4.3 Example of some bases and their combination colours with various naphthols

Bases	Structure	Coupling rate	Group	Colour produced with various naphthols						
				AS	AS-G	AS-SW	AS-D	AS-BR	AS-BG	
Scarlet GG		Rapid	Group 1	Bright yellowish red	Bright yellow	Bright yellowish red	Bright orange	Reddish brown	Brown	
Orange GC		Medium	Group 1	Bright red	Bright yellow	Bright yellowish red	Yellowish red	Reddish brown	Reddish orange	
Red TR		Medium	Group 2	Bright red	Bright yellow	Bright red	Yellowish red	Reddish brown	Dull red	
Violet B		Medium	Group 3	Bright blues violet	Reddish yellow	Dull reddish violet	Dull violet	Dull bordeaux	Bluish red	
Garnet GBC		Slow	Group 1	Dull bordeaux	Yellowish orange	Dull bordeaux	Dull reddish violet	-	Dull bordeaux	
Scarlet RC		Medium	Group 1	Bright red	Yellow	Bright red	Bright red	Reddish orange	Bright red	

naphthols. There are two methods for the dissolution of naphthol, namely, hot and cold dissolution methods.

#### 4.5.2 Naphtholation

The treatment of textile materials with naphthol solution is called naphtholation. When cotton textiles come into contact with naphthol solution, exhaustion begins at a rate depending on the substantivity of the fibre for the naphthol. Application of naphthol may be carried out either by the exhaust technique or by the continuous method using a padding mangle. Naphthol is mostly applied to either yarn or fabric. Yarn is either dyed in a package-dyeing machine in package form or in hank form in an open beck liquor-circulating machine. For smaller lots and heavy fabrics a jigger is used for naphthol application.

Since the exhaustion of naphthol decreases with an increase in temperature, batch treatments are normally carried out at 30–40°C. If improved wetting or penetration is required the temperature may be increased to 50°C. It is essential to prepare the naphthol solution just before use, as the stability of naphthol solution and the naphtholated material is limited. 20–30 min treatment is generally the required treatment time. The effects of various types of alkali on the rate of absorption of different naphthols are discussed in the literature (Huckel, 1958). The final concentration of naphthol on the fabric or yarn may be reduced by rinsing. In continuous dyeing, excess liquor is removed by drying the fabric. Care must be taken to avoid sudden drying to prevent uneven absorption of naphthol due to migration, leading to uneven drying. Careful drying after naphthol application leads to dyeing of high fastness on development (Wiltshire, 1954).

#### 4.5.3 Development

After naphtholation and subsequent treatments such as rinsing or drying, the material passes into the development bath which contains a dilute solution of a diazonium salt. This is produced either by diazotisation of an aromatic amine, a so-called fast colour base, or by dissolving stabilised diazo fast colour salt, which is commercially available in solid form.

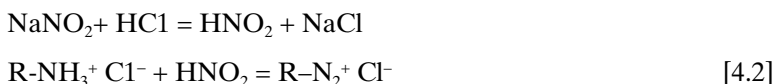
The process of converting an aromatic amine (in the present case a fast base) into its reactive form, diazonium compound, is called *diazotisation* (Hodgson and Norris, 1949). This reaction is a valuable tool not only in the application of azoic colours, but also in the synthesis of a large number of dyestuffs having azo groups.

The reaction involves two steps (Ridd, 1959). The first step is conversion of the free base into its water-soluble salt, usually hydrochloride. This is

carried out by treatment with concentrated hydrochloric acid and by heating or boiling, if necessary.



The second step is the reaction of the hydrochloride of the base with nitrous acid; this usually done at low temperature (ideally 0–5°C). Generally a temperature range of 8–12°C is economical and is achieved by adding ice into the diazotising bath. This is carried out by adding sodium nitrite into a solution of the hydrochloride of the base in the presence of excess hydrochloric acid.



Formation of a clear final solution and the absence of froth indicate successful diazotisation. The diazonium salt is unstable even at room temperature in that it reacts with water and is decomposed. This decomposition is accelerated by heat and light. Contact with metal surfaces also encourages decomposition of the salts so the diazotisation reaction should not be carried out in metal containers.

Both hydrochloric acid and sodium nitrite/nitrous acid should be present in sufficient quantities during diazotisation. The presence of hydrochloric acid is confirmed by Congo Red paper, which turns blue when dipped in the solution. A starch-iodide paper turns blue, if nitrous acid is in excess.

#### 4.5.4 Properties of azoic colours

The wash-fastness properties of azoic dyed cellulosic materials are excellent. All azoic combinations withstand soaping at the boil. The dark shades exhibit excellent light-fastness. However, at medium and pale shades light-fastness is good to fair. Like many other dyes, the light-fastness of azoic dyed ground fabric or yarn is also affected by environmental humidity. Unlike sulphur dyes most of the azoic pigment withstands chlorine bleaching. In India, for example, azoic dyed coloured yarns are used for borders during weaving cheaper quality materials, especially saris. These woven fabrics may be bleached with chlorine containing bleaching agents without any danger of colour removal. Most of the azoic combinations have excellent perspiration-fastness also. Fastness to hydrogen peroxide is not adequate. Many organic solvents affect most of the azoic dyed shades. Rubbing-fastness problems are very common with azoic colours; this problem can be overcome by adopting proper dyeing technology (see Section 4.7).

The dischargeability of azoic colours is good; hence they are suitable for dyed ground shades intended for white or coloured discharge prints. The use of azoic colours has declined since the introduction of reactive dyes and the subsequent developments of this dye class. Since many of the components used in naphthol dyeing are known or suspected carcinogens, they should not be used. During selection of an ACC and azoic diazo component, care should be taken and it is advisable to consult materials safety data sheets.

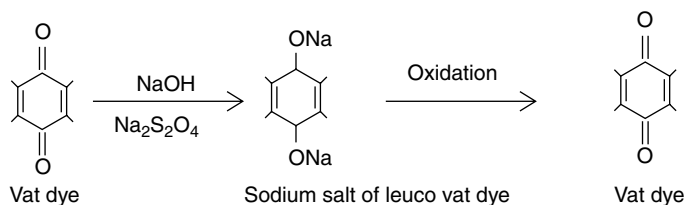
## 4.6 Fundamental principles of vat dyeing

### 4.6.1 Chemistry of vat dyes

Use of a vat dyestuff is traced to ancient times: a blue colouring matter known as 'Indigo' is one of the oldest naturally occurring vat dyes and has been known to Indian people for more than 5000 years (Aspland, 1997). Indigo was first recovered from glucoside indican, naturally found in the plants *Indigofera tinctoria* in India (called *Neel* in the Indian language). The leaves of the plant were soaked in water and fermented in order to convert the glycoside indican into blue dye indigotin. The natural fermentation process later became known as vatting – this is basically a reduction process. The industrial use of vat dyes started at the beginning of the twentieth century.

Vat dyes are insoluble in water and are available in powder, liquid and paste form. Organic solvents are used for producing the liquid form. For the powder brand of dyes, particle size plays an important role in governing the dissolution and other dyeing related properties (Johnson, 1989). Vat dyes with very few exceptions fall into two clearly defined groups, namely indigoid and anthraquinonoid. The former group includes indigo, thioindigo and their derivatives, while the later includes derivatives of anthraquinone as well as heterocyclic quinines. The structure of indigo was first proposed by von Baeyer. A question that has intrigued colour chemists for years is how indigo, a relatively small molecule, absorbs at such long wavelengths. The colour developed by indigo is highly dependent on which state and environment it is present in. In the vapour phase it is red where it exists as a monomolecular state. In a polar solvent it is blue while in a non-polar solvent it is violet. When it is applied to textiles as vat dye in a solid state it is blue (Christie, 2001).

The anthraquinonoid vat dyes are characterised by having five to ten aromatic rings, many of them condensed together. The structures of anthraquinonoid vat dyes fall into four principal subgroups: violanthrones, anthraquinone carbazoles, indantrones and benzanthrone acridones. These compounds are characterised as the ketonic group, which on reduction forms a leuco compound (Fig. 4.19). In the presence of sodium hydroxide



4.19 Chemical reactions involved in vat dye application.

Table 4.4 Vatting and dyeing conditions for various groups of vat dyes

Group	Temperature (°C)		Dyebath chemicals (g/L)		
	Vatting	Dyeing	Caustic	Hydrosulphite	Sodium sulphate
IK	50	20–30	0.4–3.0	0.4–4.5	12.0
IW	50	40–50	0.4–4.5	0.4–6.5	12.0
IN	50–60	50–60	1.5–10	1.5–10	nil
IN special	Dyes requiring individual treatment				

the leuco form is converted into sodium salt and thus confers solubility to the dyes. The dyes are applied to the textile materials in this form and after the completion of dyeing, the soluble form of the dye is oxidised back to the parent insoluble form.

Although the major vat dyes are very complex systems, their synthesis from smaller molecules tends to be rather simple, for example by condensations or oxidative cyclisations. There are some anthraquinonoid vat dyes that contain sulphur in their structure. These compounds may be applied to cellulosic materials either by a vat dyeing process or a sulphur dyeing process. These categories of dyes are known as sulphurised vat dyes.

#### 4.6.2 Classification of vat dyes

Vat dyes may be classified in a number of ways. One popular method of classification divides into four subgroups: IK, IW, IN and IN special. The members of these groups differ in the affinity of their leuco compounds towards cellulosic materials and the corresponding differences in dyeing temperatures and the salt, caustic soda and sodium hydrosulphite concentrations necessary to have the optimum dyeing effect. The I stands for Indanthrene and has been a trademark for vat dyes since the synthesis of indanthrone, and the name Indanthrene has been used as a synonym for vat dyes since then.

K stands for cold (*kalt* in German); dyes belonging to this group are dyed at room temperature with a comparatively high concentration of electrolyte and a relatively low caustic soda concentration (Table 4.4). W stands for

warm; dyes in this group can be applied using less salt and slightly more alkali. They are applied at slightly higher temperature than IK dyes. N stands for normal; these dyes require more alkali and no electrolyte. The dyeing temperature of these dyes is higher than for the IW class. The dyeing is performed at 60–65°C.

Each member of IN special class requires individual treatment. Dye manufacturers' instructions should be followed in such cases. For compound shades, dyes from the same group should preferably be selected. If dyes from IW and IN are required to be mixed, the conditions for IN should be maintained.

### 4.6.3 Properties of vat dyes

Vat dyes are substantive towards the fibre only when they are converted to soluble leuco compounds, which are obtained as a result of treatment with sodium hydrosulphite (reducing agent) in presence of caustic soda solution. The leuco compounds are often colourless or of quite a different colour from the product of oxidation. The leuco compounds are usually present in the dye liquor in a monomolecular form or as aggregates of a few dye molecules. Valko (1941) investigated the aggregation behaviour of leuco vat dyes from their diffusion studies and concluded that they remain in an aggregate of two to four molecules. The substantivity of a dye for the fibre is determined by its constitution and is unaffected by the degree of aggregation. The aggregation can, however, affect the diffusion and migration properties of the dyes. Hence levelling of the shade is adversely affected due to the aggregation of the dyes. Certain leuco dyes, called tenderers, can damage the fibre if there is frequent alteration of oxidation and reduction during the dyeing process. The problem can be tackled by the addition of pyrocatechol or tannin (Shore, 1995).

After the completion of dyeing, the dyes are oxidised back to the original insoluble form. The large vat dye molecule is trapped within the polymer system of the fibre because of its size and aqueous insolubility and it is absorbed within the fibre polymer system by van der Waals forces. The excellent wash-fastness of vat dyes is attributed to the aqueous insolubility and large size of their molecules. The wash-fastness rating of vat dyes is about four to five. The light-fastness rating of vat dyes is about seven. The maximum light-fastness rating of textiles coloured with vat dyes is attributed to the stable electron arrangement in the chromophores of the vat dye molecules. Therefore, dyes having a multinuclear ring system within the NH group are particularly fast to light. However, in certain combination shades due to catalytic fading, one of the components gets faded fast on exposure to light. Vat-dyed cellulosic materials are more easily degraded

in light compared with undyed ones. Reduction of vat dye present in the material followed by its oxidation by atmospheric oxygen produces certain peroxides which oxidise the fibre. This is particularly found with dyes able to absorb light of short wavelengths.

As well as having fastness to washing and light, vat-dyed materials have excellent fastness to mercerisation, scouring with soda, chlorite and hypochlorite bleaching. Because of their excellent fastness to all these pre-treatment processes, vat dyes are considered as ideal dyes for dyeing yarns to be used in manufacturing coloured woven goods like shirts, handkerchiefs, towels, some sari borders, etc.

Some of the dyes like flavanthrone, pyranthrone and violanthrone dyes are sensitive to alkaline washing at high temperature. An increase in molecular size and the number of reducible keto groups can tackle the problem. Addition of a mild oxidising agent like sodium meta nitrobenzene sulphate in the washbath can minimise the defect.

Vat dyes have always been very expensive compared with other dye classes and are used for high-quality products only.

#### 4.6.4 Principles of vat dye application

Vat dyes can be applied by three major techniques: exhaust, semi-continuous and continuous methods.

##### *Exhaust dyeing*

Exhaust dyeing with vat dyes takes place in the following four steps:

1. Solubilisation of the vat dye, i.e. conversion of the dye to sodium salt of leuco acid through the vatting process.
2. Application of the soluble dye to the textile material, i.e. dyeing.
3. Oxidation of the dye back to the parent insoluble form.
4. After-treatment or soaping.

Before the actual dyeing operation, the water-insoluble dye must be converted into the water-soluble substantive form. This is achieved by vatting, i.e. reduction with a reducing agent, usually sodium hydrosulphite in the presence of sodium hydroxide to form sodium salt of leuco compound (Fig. 4.19). Addition of caustic soda prior to the addition of sodium hydrosulphite ensures complete conversion of the vat dye to sodium salt of leuco acid (Etters, 1989). It is observed that the higher the concentration of reducing agent and dye, the more rapidly reduction takes place. To keep the dye in the dissolved state during vatting and dyeing, both the reducing agent and caustic soda should remain in adequate quantities. The presence of



hydrosulphite and caustic soda is tested by a change in colour of vat yellow paper to blue and phenolphthalein to pink, when brought in contact with the solution.

The vatted dye solution can be added to a dyebath containing the required amount of caustic soda and sodium hydrosulphite and kept at the recommended temperature (Table 4.4). The various factors which affect the vating efficiency and ease are the particle size of the dye powder, reduction potential and pH. The smaller the size of the particles, the more easily the dye gets reduced. The ease of reduction of vat dyes can be expressed in terms of reduction potential. Vating rate is not found to be related to the leuco potential of the dyes (Baumgarte, 1987).

Vat dyes are available in highly fine powder form, which when added to water form a dispersion of very fine particles. This is then added to a dyebath in which it is reduced and brought into solution, thus eliminating the necessity for vating as a separate step. In the second step, which is the actual dyeing step, the sodium salt of leuco vat dye is absorbed on the surface of fibre, from where it diffuses into the interior of the fibre. The adsorption and diffusion of the dye is only possible when it is in soluble substantive form. Hence, the addition of excess quantities of both sodium hydrosulphite and caustic are essential.

After the completion of the exhaustion process the dyed material is rinsed to remove superficially held dye particles and any residual reducing agent and alkali. The leuco dye is then reconverted into its original form by oxidation. This is carried out with hydrogen peroxide or sodium perborate, or more recently sodium metanitrobenzene sulphonate.

Other methods of oxidation are also available such as treatment with hypochlorite, potassium dichromate and acetic acid, or treatment with sodium chlorite, but these are not recommended due to their environmental effects. After oxidation the dyed materials are treated in an aqueous solution of surfactant at boiling temperature. This last step is considered a very important step in vat dyeing. Proper soaping treatment removes the loose dyes and enhances the fastness properties by aggregation and orientation of the dyes inside the fibre.

### *Semi-continuous dyeing process*

With the introduction of very fine particles of vat dyes by dye manufacturers, it is now possible to effect a uniform deposition of dyestuff particles in a non-substantive form on fabric using a padding mangle (pigmentation). In this process the fabric is first padded with an unvatted microfine dye dispersion and subsequently dried in a drier. The colour is then developed on a jigger using the standard concentration of sodium hydrosulphite and caustic soda. The fabric can also be developed without intermediate drying, by the wet-on-wet application method. For pale and light shades, the drying

step may be bypassed. Drying is an expensive phenomenon in processing. The greater the number of drying steps the higher the cost of production will be. Thus there is always a trend to cut down the number of drying steps, although intermediate drying gives better results over wet developments.

### *Vat acid process*

In this method the dye is first vatted as discussed earlier. The alkali present in the solution is gradually neutralised with the addition of acetic acid and constant stirring in the presence of a dispersing agent. Due to the neutralisation of the alkali, fine particles of insoluble leuco acid are formed, which remain in a dispersed state in the mixture. If the acetic acid is insufficient to neutralise all the alkali present in the solution, vat acid is not formed. If the dispersing agent is not adequate, the vat acids formed *in situ* will get precipitated. Therefore quantities of both these chemicals are important. The dispersion is then applied to the fabric by padding. The dyes on the fabric are then developed on a jigger as described in the previous method, with or without intermediate drying. Both the semi-continuous methods can be applied to dye yarn in a yarn package-dyeing machine.

The advantages of the vat acid process over the pigmentation process are as follows:

- (i) Unlike the pigmentation method, any form of vat dyes can be used in the vat acid process. The method is not only restricted to microfine powder forms.
- (ii) Vat acid dispersion is much finer than dispersion prepared from micro-powder brands. The very fine particle size of vat acids helps considerably in the penetration into the fabric.
- (iii) The vat acid process is marked by the rapid speed of development, which cuts down the bleeding of dyeing in the developing bath.

### *Continuous dyeing process*

The sequence followed in this case is as follows:

Pad (pigment) – Dry – Chemical pad – Steam – Oxidation and soaping in a continuous open soaper.

The fabric is padded with vat pigment dispersion. The addition of a wetting agent and an anti-migrating agent may be necessary. The addition of these chemicals may be avoided by proper pre-treatment of the fabric. The fabric is preferably dried in a hot flue drier.

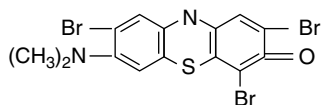
The dried fabric is cooled before its introduction into the chemical pad bath where it is treated with a reducing agent and caustic soda. To prevent

bleeding of colour, common salt or pad liquor may be added in the chemical pad bath. The fabric, after chemical padding, should be immediately steamed for 30–40 s at 102–104°C. The wet-on-wet method may also be used for medium to light-weight fabrics. Continuous dyeing is economical particularly where long yardages have to be dyed in the same colour.

## 4.7 Fundamental principles of sulphur dyeing

### 4.7.1 Chemistry of sulphur dyes

These are so called because they contain sulphur atoms in their molecules (Fig. 4.20). The fibres most readily coloured with sulphur dyes are natural and man-made cellulosic fibres. The first dye of this class, Cachou de Laval, was obtained in 1873 by heating organic waste like sawdust with alkali and sulphur (Shore, 1990). Therefore, the first sulphur dye was discovered before direct dyes, but it was not until the development of the sulphur blacks that this class of dyes made a major impact on cotton dyeing. These dyes are the most commonly used dyes manufactured for cotton in terms of volume. They are cheap, generally have good wash-fastness and are easy to apply. Dark colours such as blacks, browns and dark blues are economically produced with sulphur dyes. The deep indigo blues of denim jeans are a product of sulphur dyes. Sulphur dyes are water-insoluble. The insoluble sulphur dyes are first converted into a soluble form by treatment with an alkaline reducing agent; after this the soluble dye has substantivity towards the fibre. After dyeing the dye is oxidised back to its original form. They are principally mixtures of coloured compounds and because of their insolubility in nearly all solvents, their constitutions have never been completely unveiled. They do not have well-defined chemical structures. They are mostly dull and exist in a highly polymeric state. The colour developed by these dyes is the resultant colour of more than one component and hence a sharp absorption band is hardly ever achieved. Sulphur dyes do not have any pure red colour in their shade range. A pink or lighter scarlet colour is available. Sulphur dyes are generally produced by sulphurisation or thionation of aromatic hydrocarbons containing hydroxy, nitro and/or amino groups. Sulphurisation is usually carried out by different methods, such as by heating dry with sulphur or sodium polysulphide or by boiling in a solvent like butanol, cellosolve or



4.20 C.I. Sulphur Blue 9.

dioxitol under reflux, or under pressure at temperatures up to about 150°C. The type of method and reagent is used to control the constitution, colour and fastness properties of the products. Many yellow, orange and brown sulphur dyes are made by dry baking of intermediates such as 2,4-diaminotoluene with sulphur above 160°C.

#### 4.7.2 Classification of sulphur dyes

Sulphur dyes are available in different commercial forms such as powder, pre-reduced powders, grains, dispersed powders, pastes, liquids and also as water-soluble forms. As the structures of sulphur dyes are not well-defined they are best classified by their application methods. They may be divided into three main subgroups as follows.

##### *C.I. sulphur dyes*

These are water-insoluble dyes, containing sulphur both as an integral part of the chromophore and in attached polypeptide chains. They are normally applied in the alkaline-soluble reduced (leuco) form from a sodium sulphide solution, and after the application they are converted back to their original form by oxidation. Sulphur dyes are easily reducible dyes compared with vat dyes but their reoxidation is difficult.

##### *C.I. leuco sulphur dyes*

This class of dyes is available in either powder or liquid form. They normally contain conventional dye with sufficient reducing agent which makes them suitable for direct application. This class is best suited for the single bath, pad steam process.

##### *C.I. solubilised sulphur dyes*

This class of sulphur dyes are chemically different from the previous two as they are thiosulphuric acid derivatives of the parent dye. They are readily soluble in water but possess no substantivity to cellulosic fibres until reduced in the presence of an alkali. They can be applied by exhaust as well as the pad dry-steam method.

#### 4.7.3 Principles of sulphur dye application

The principles of application of sulphur to cotton are the same as those for vat dyes. The process consists of four steps including reduction of the dye to make it soluble, application of the dye, i.e. dyeing, oxidation of the absorbed

dye in the fibre and finally rinsing or quick washing. Sodium sulphide is a commonly used reducing agent. This principle of application of sulphur to cotton is inexpensive but not free from environmental problems. Discharge of sulphides in the effluent system has many disadvantages like corrosion of sewerage systems, damage to treatment works, high pH, significant effects on aquatic life downstream, damage to the DNA of tadpoles, etc. Recent advances in dyeing technologies have allowed the substitution of toxic sulphide reducing agents. Thiourea dioxide is a better choice from an ecological point of view but significantly more expensive than sodium sulphides. Glucose is now used and both low sulphide and zero sulphide products are available. Future developments in the field of reducing dye levels by means of electrochemical processes are promising.

#### 4.7.4 Properties of sulphur dyes

The shade range for sulphur dyes is mainly limited to black, brown, blue and olive. Sulphur dyed materials look dull, they exhibit fair-to-good wash-fastness properties and fair light-fastness. Exposure of the dyed material to UV light causes degradation of the chromophoric part. These dyes generally exhibit good to excellent fastness to alkaline perspirations whereas they have fair-to-good fastness towards acidic perspiration. Sulphur dyes themselves have a relatively low detrimental environmental impact as the dyes are free from heavy metals and Adsorbable Organic Halides (AOX). Most of the sulphur dyes are reduced by sodium sulphide. Discharge of sulphides is only permissible in very small amounts (usually the legal allowance is 2 ppm). Research has been conducted to find suitable alternative reducing agents for sulphur dyes. Some of the alternatives suggested are the use of thiourea dioxide, glucose and the cathodic reduction process.

### 4.8 Conclusions

The textile industry is one of the important industries in the world. World demand for dyes and organic pigments is forecast to increase 3.9% per year to \$16.2 billion in 2013.

For economical, eco-friendly and efficient dyeing of textiles materials some of the important points to be taken into account are the (a) selection of class of dye; (b) environmental effects and safety data of the dyes and chemicals to be used; (c) selection of method of dyeing; (d) laboratory trials to get proper shades; (e) minimum variation of process parameters to avoid lot-to-lot variation and (f) proper after-treatment to get maximum fastness properties.

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## Thermodynamics and kinetics of dyeing and dyebath monitoring systems

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**Abstract:** The chapter provides an introduction to the physical chemistry of dyeing. Traditionally, scientific analysis distinguishes between systems in equilibrium, when they fall into the domain of thermodynamics, and dynamic systems. Both types of analysis, thermodynamic and kinetic, are relevant for dyeing processes and will therefore be explained. Dyebath monitoring systems have helped in the scientific analysis of dyeing processes and have become popular in industry, too. Their technical features, performance limits and scope for future developments are reviewed in the later part of the chapter.

**Key words:** Gouy–Chapman, Donnan, kinetics, diffusion, dyebath monitoring systems.

### 5.1 Introduction

The chapter provides an introduction to the physical chemistry of dyeing, a discipline which thrived after the publication of Vickerstaff's classical book in the 1950s (Vickerstaff, 1954). Traditionally, scientific analysis distinguishes between systems in equilibrium, when they fall into the domain of thermodynamics, and dynamic systems. Both types of analysis, thermodynamic and kinetic, are important for understanding of dyeing processes and will be explained.

Dyebath monitoring systems have helped in the scientific analysis of dyeing processes and have become popular in industry, too. Their technical features, performance limits and scope for future developments are reviewed in the later part of the chapter.

### 5.2 Thermodynamics of dyeing

Chemical thermodynamics analyses the interrelation of energy with chemical reactions and apply to a system in its equilibrium state, which is reached when a system's macroscopic variables such as temperature, pH value, dye concentration in the bath and dye amount on the fibre, etc., do not change



any more with time. Thermodynamics may provide answers concerning the final value of these parameters, not necessarily the speed with which the final value is reached.

As far as dye–fibre systems are concerned, the equilibrium dye uptake is an important variable. It is not only of theoretical interest but also of practical importance since under industrial conditions dyeing equilibrium is usually reached, in good approximation, at the end of the process. Thus, colour reproducibility under industrial conditions is linked to questions of chemical thermodynamics.

### 5.2.1 Affinity and substantivity

There are at least two different hypotheses explaining why dyes have affinity for fibres. One is based on chemical attractions (e.g. ion–dipole interaction, hydrogen  $\pi$ -bonds, acid-base bonds or dispersion forces), the other is based on mechanical effects due to the pore structure of the substrate (Ingamells, 1989; Shore, 2002, p. 116).

The standard affinity,  $\Delta\mu^0$  [ $\text{J}\cdot\text{mol}^{-1}$ ], is defined for thermodynamically reversible systems, such as cotton and direct dyes, as a measure of the tendency of the dye to move from its standard state in the dye solution to its standard state in the fibre (Burdett, 1989). It can be regarded as the driving force of the dyeing process, i.e. a dye with higher affinity will have under normal circumstances a stronger tendency to accumulate on the fibre.

The affinity may be calculated from the chemical potentials of dye molecules within the fibre,  $\mu_f$ , and within the solution,  $\mu_s$ . The chemical potential is an intensive quantity that represents an increase in the Gibbs free energy resulting from the addition at constant temperature and pressure of one mol of a component to such a large quantity of the system that its composition remains virtually unchanged (Burdett, 1989). At equilibrium,  $\mu_f$  is equal to  $\mu_s$ :

$$\mu_f = \mu_s = \mu_f^0 + RT \ln a_f = \mu_s^0 + RT \ln a_s \quad [5.1]$$

The subscript ‘f’ refers to the fibre and the subscript ‘s’ refers to the solution. The standard affinity can then be defined as

$$\Delta\mu^0 = (\mu_f^0 - \mu_s^0) = -RT \ln \frac{a_f}{a_s} \quad [5.2]$$

For physicochemical processes, which include change of state and change of location, i.e. dyeing processes, the activities can be related to amounts of

products and reactants if it is assumed that the laws governing ideal gases hold. It follows (Breuer and Rattee, 1974, p. 43) that:

$$-\Delta\mu^0 = RT \ln K \quad [5.3]$$

where  $K$  is the dimensionless equilibrium sorption constant.

The affinity should be a constant for a particular dye and a particular substrate at any one temperature (Sumner, 1989).<sup>\*</sup> In the case of a direct dye on cotton or of an acid dye on nylon, for example, it should therefore be possible to predict the amount of sorbed dye at equilibrium for varying dye amounts, electrolyte concentrations and pH values from the value of the affinity, if known. Hence the main objective of mathematical models of equilibrium dye sorption is to quantify the affinity of a dye for a certain substrate, preferably in such a way that all the predictor variables in the equation can be determined experimentally.

Substantivity is sometimes used synonymously with affinity (Vickerstaff, 1954, p. 173). More recently, however, it has been defined as 'the attraction between a substrate and a dye or other substance under the conditions of test whereby the latter is selectively extracted from the application medium by the substrate' (Sumner, 1989). This definition accentuates that the substantivity varies with application conditions and would normally not be a constant at constant temperature. It is suggested here to use the term 'substantivity' with the latter meaning.

Due to the exothermic nature of the dye sorption, dye affinity drops with temperature and so does the amount of sorbed dye, all other factors remaining constant. The thermodynamic quantity that predicts the fall in the affinity is the standard enthalpy of dyeing,  $\Delta H^0$  [J.mol<sup>-1</sup>], also called heat of dyeing. It may be defined as the thermal energy released when dye is transferred from its standard state in solution to its standard state on the fibre (Sumner, 1989). Provided that  $\Delta H^0$  is a constant, independent of the temperature  $T$ , it can be related to the standard affinity

$$\Delta H^0 = \frac{d(\Delta\mu^0/T)}{d(1/T)} \quad [5.4]$$

The standard enthalpy can be obtained from experimental results by plotting  $\Delta\mu/T$  against  $1/T$  or by linear regression of the two parameters.

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<sup>\*</sup> This statement is not uncontested. Several authors have found that dye-fibre interactions increase at low dye concentrations, leading to an increased affinity (Daruwalla and D'Silva, 1963; McGregor, 1972; Vickerstaff 1954, p. 233).

## 5.2.2 Sorption isotherms

A classical method to express the results of equilibrium sorption experiments, not only in textiles, is to plot the equilibrium amount of ‘product’ against the amount of ‘reactant’, i.e. the dye molality on the fibre against the concentration in solution at constant temperature, the sorption isotherm (Vickerstaff, 1954, p. 97). Note that the term ‘molality’ refers to the amount of substance of solute divided by the mass of solvent and is usually expressed in  $\text{mol.kg}^{-1}$ . The term ‘concentration’ refers to the amount of substance divided by the volume of solvent and is usually expressed in  $\text{mol dm}^{-3}$ . For textile applications, three types of isotherms are often encountered: Nernst, Freundlich, Langmuir.

Each of the three types can be linked to a certain sorption mechanism. Even so, it may be noted that a good fit between experimental data and a particular isotherm-type does not imply that the underlying mechanism is identical to the one suggested by the model!

### *Nernst isotherm*

In the case of a Nernst isotherm, the equilibrium dye molality on the fibre,  $[D]_{f,\text{eq}}$ , is a linear function of the dye concentration in the bath,  $[D]_{s,\text{eq}}$ , until the fibre saturation molality is reached.

$$[D]_{f,\text{eq}} = K[D]_{s,\text{eq}} \quad [5.5]$$

The proportionality constant,  $K$ , is called partition coefficient (Aspland, 1997, p. 176). The equation can be derived from the kinetics of the reversible adsorption of ideal gases (Breuer and Rattee, 1974, p. 33). This type of isotherm indicates that the fibre behaves as a solvent for the dye. The sorption of disperse dyes on polyester, acetate or nylon can often be described in such a form (Aspland, 1997, p. 176).

### *Freundlich isotherm*

In most dye–fibre systems, the partition coefficient decreases at increasing dyebath concentrations. This decrease may have many reasons (Aspland, 1997, p. 19; Breuer and Rattee, 1974, p. 34). For example, the dye’s activity in solution could be diminished at higher concentrations due to aggregation or the fibre surface could be heterogeneous, so that dye–fibre interactions in some early filled locations are stronger than in others.

Freundlich isotherms are of the general form

$$[D]_{f,\text{eq}} = K[D]_{s,\text{eq}}^n \quad [5.6]$$

where the exponent,  $n$ , is an empirical constant between zero and one. Dyeing systems usually have values of ' $n$ ' of around 0.5 (L Peters, 1975). Although the equation was originally purely empirical in nature (Freundlich, 1907), equations of this type can be derived mathematically from the assumption of certain heterogeneous surfaces (Breuer and Rattee, 1974, p. 34). One characteristic of the equation is that no saturation value is attained so that the dye amount on the fibre keeps increasing with the concentration in solution.

The experimental results of direct dyeings on cellulose are often interpreted by assuming a Freundlich isotherm (Vickerstaff, 1954, p. 227; Willis *et al.*, 1945). It has also been successfully used to distinguish between effects on equilibrium sorption of pre-treatment and fibre provenance on the one hand and dyeing conditions on the other (Elgert *et al.*, 1989).

There are two important drawbacks when Freundlich isotherms are employed. First, it is difficult to relate the coefficients to fundamental values such as the dye's affinity (L Peters, 1975). This reduces the capability to accurately predict dye uptake at values different from the ones employed in the original experiments. Second, saturation effects of the fibre are neglected. The second aspect is taken into account in a Langmuir isotherm.

### *Langmuir isotherm*

The Langmuir isotherm was originally derived to describe the adsorption of gases on metal surfaces (Langmuir, 1916). It assumes that there are a limited number of sorption sites,  $[D]_{\text{sat}}$  [mol.kg<sup>-1</sup>], and that the sorption speed is proportional to the number of unoccupied sites as well as to the concentration of the molecules in contact with the solid phase. These assumptions yield the following equation:

$$[D]_{\text{f,eq}} = \frac{K[D]_{\text{sat}}[D]_{\text{s,eq}}}{1 + K[D]_{\text{s,eq}}} \quad [5.7]$$

It has been argued that competition for sorption places cannot be important for cotton dyeing as the fibre is normally far from being saturated. Experiments with direct dye mixtures have shown, however, that a Langmuir-type isotherm yielded better agreement with experimental data than a Freundlich-type isotherm (Gerber, 1996; Porter, 1992). This supports the suggestion that there is dye competition for sites at the fibre surface.

One of the difficulties in using the Langmuir approach is to calculate the dye saturation molality of the fibre. Due to the lack of specific sorption sites on cellulose for the dye anions, for example, there is no clear theoretically predictable maximum dye uptake or saturation value. A common way to

calculate the saturation value from experiments is to plot the inverse of the dye molality on the fibre against the inverse of the dye concentration in solution and determine the intersection with the  $y$ -axis by linear regression and extrapolation (Burdett, 1989).

The three types of isotherm may be combined to better reflect experimental results. A combination of a Langmuir and Nernst isotherm, for example, can be used to express the characteristics of acid dyeings on wool, on silk and on nylon (Aspland, 1997, p. 252).

None of the models discussed so far explicitly takes into account ionic interactions between dye and fibre. This, and the difficulty of relating these isotherm equations to more fundamental thermodynamic properties, make an extension of the models desirable. Two theories often used to express electrical effects are the Donnan membrane equilibrium model and the Gouy–Chapman model.

The Donnan and the Gouy–Chapman models quantify the effect of the ionic interaction between fibre and dye. When, for example in the case of cotton, the fibre is immersed in a dyebath the surface assumes a negative charge due to the adsorption of dye anions and ionic groups on the fibre itself. The negative charge attracts counter-ions which accumulate in the dye solution adjacent to the fibre surface. The excess of cations over anions gradually diminishes with increasing distance from the fibre surface. The resulting electrical potential has to be overcome by the negatively charged dye ions when they approach the fibre. The potential difference important for the dyeing process is between the electrical potential at the point of dye adsorption at the fibre surface and at the point in the dyebath far away from the fibre.

The effect of the electrical potential difference,  $\Psi_0$  [V], has to be included in the calculation of the affinity so that Equation [5.3] becomes (Burdett, 1989)

$$-\Delta\mu^0 = RT \ln K + zF\Psi_0 \quad [5.8]$$

In case a Nernst isotherm is assumed ( $K = [D]_f \cdot [D]_s^{-1}$ ) the result is

$$-\Delta\mu^0 = RT \ln \frac{[D]_f}{[D]_s} + zF\Psi_0 \quad [5.9]$$

The Donnan and the Gouy–Chapman model represent two methods to calculate  $\Psi_0$ .

### 5.2.3 Donnan model

The Donnan method is based upon the assumption that the distribution of ions is determined by a membrane potential that has exclusively electrostatic

origins. Other effects, such as spatial constraints that could play a role in the ion distribution are therefore not considered. The membrane potential is created by the fact that some ions cannot freely move, while others can. Fixed charges may be caused by ionised hydroxyl- and carboxyl- or amine-groups of the fibre, for example.

In the simplest case, the system is divided into two parts, the bulk solution and the fibre surface layer, which is also called the internal solution. In the two-phase model the sorbed molecules are considered dissolved in the surface layer which lacks specific adsorption points, hence also the term 'diffuse adsorption'. The Donnan model of diffuse adsorption has been widely used to describe the sorption of dyes on cellulose (R H Peters, 1975; Sumner, 1989).

The Donnan model interprets  $\Psi_0$  as the potential difference between the internal solution and the bulk solution.  $\Psi_0$  can be related to the newly introduced Donnan coefficient of distribution,  $\lambda$  [-], which describes the partition of ions between the internal (subscript i) and the bulk solution (subscript s):

$$\Psi_0 = -\frac{RT}{F} \ln \lambda \quad [5.10]$$

Substituting Equation [5.10] in Equation [5.9] yields

$$-\Delta\mu_0 = RT \ln \left( \frac{[D]_i}{[D]_s} \frac{1}{\lambda^z} \right) \quad [5.11]$$

In the simplest case a dye  $\text{Na}_z\text{D}$  fully dissociates into  $z$   $\text{Na}^+$ -ions and one  $\text{D}^{z-}$ -ion and the only other ions present are  $\text{Na}^+$ -ions and  $\text{Cl}^-$ -ions from sodium chloride. Since the chemical potential in the bulk solution is equal to that in the internal solution the following Donnan relationship applies (ionic charges are omitted for simplicity):

$$[\text{Na}]_i^z [D]_i = [\text{Na}]_s^z [D]_s \quad [5.12]$$

Then  $\lambda$  is

$$\lambda^z = \frac{[\text{Na}]_s^z}{[\text{Na}]_i^z} = \frac{[D]_i}{[D]_s} \quad [5.13]$$

and the affinity becomes

$$-\Delta\mu_0 = -RT \ln \left( \frac{[\text{Na}]_i^z [D]_i}{[\text{Na}]_s^z [D]_s} \right) \quad [5.14]$$

For the equation to be dimensionally correct, the two amounts on the fibre,  $[Na]_f$  and  $[D]_f$ , must be expressed in amount per volume of internal solution (i.e. the volume of the surface layer) rather than amount per fibre mass. This can be achieved by division of  $[Na]_f$  and  $[D]_f$  with the so-called internal volume of the fibre,  $V$ , which quantifies the volume of internal solution per kilogram of fibre.

The internal volume can be interpreted as the total micellar fibre surface accessible to the dye (Vickerstaff, 1954, p. 216) or the volume of the diffuse electric double layer adjacent to the fibre surface (Sumner, 1989). The volume is a function of the accessibility of the fibre surface to the dye molecules, i.e. the better the accessibility of the fibre surface, the higher the internal volume. For different types of cellulose, for example, values between 0.22 and 0.65 dm<sup>3</sup>.kg<sup>-1</sup> have been determined experimentally (Sumner, 1989).

In order to take into account saturation effects on the fibre surface and dye competition for adsorption sites, the two-phase Donnan model of diffuse adsorption can be extended to a three-phase model dividing the dye–fibre system into three phases: fibre, bulk solution and internal solution next to the fibre surface (Porter, 1992). It is usually presumed that specific adsorption sites exist for the dye molecules, whereas the inorganic ions are adsorbed diffusely according to the Donnan equilibrium (Daruwalla and D’Silva, 1963; Weedall, 1981, p. 41). The three-phase model may be combined with different adsorption mechanisms. In the case of a constant partition coefficient (Nernst), essentially identical results as in the diffuse adsorption are obtained (Hanson *et al.*, 1935). The case when dye adsorption on the fibre is assumed to occur according to a Langmuir-type mechanism has been exemplified by applying the three-phase model to mixtures of two direct dyes (Porter, 1992).

In real dyeing systems, there are more ions to be taken into account than the dye anion, the corresponding cation and the added electrolyte. First, commercial dyes and electrolyte contain impurities that are often ionic in nature. Second, the substrate may also contain electrolyte, originating, for example in the case of cotton, from the cultivation and from alkaline or acidic pre-treatment. Furthermore, the degree of ionisation of the fibre’s ionic groups is pH dependent.

#### 5.2.4 Gouy–Chapman model

The Gouy–Chapman model provides an alternative mathematical treatment of the diffuse electric double layer. It regards the fibre as a flat and uniformly charged surface with an electrical potential and the dye anions are considered to be point charges (Burdett, 1989). The concentration of

dyes in the double layer is determined by competition between the effects of the potential field and the kinetic energy of the ions. The thickness of the double layer is expressed as Debye length,  $r_D$ , i.e. the distance from the surface where the potential has fallen to  $e^{-1}$  of the potential at the surface.

In the Gouy–Chapman model, the initial charge density of the fibre surface,  $\sigma_0$  [ $C.m^{-2}$ ], is gradually increased by dye adsorption. For a one-dye solution the charge density of the fibre,  $\sigma$ , is (Gerber, 1990)

$$\sigma = \sigma_0 + \frac{Fz[D]_f}{A} \quad [5.15]$$

The surface charge gives rise to the electrical potential,  $\Psi_0$ :

$$\psi_0 = \frac{r_D \sigma}{\epsilon_0 \epsilon} = \frac{r_D \left( \sigma_0 + \frac{Fz[D]_f}{A} \right)}{\epsilon_0 \epsilon} \quad [5.16]$$

By substituting Equation [5.16] in Equation [5.8], the affinity becomes:

$$\begin{aligned} \Delta\mu^0 &= -RT \left( \ln \frac{[D]_f}{[D]_s} + A_1 r_D + A_2 r_D z [D]_f \right) \\ A_1 &= \frac{zF\sigma_0}{RT\epsilon_0\epsilon} \\ A_2 &= \frac{zF^2}{RT\epsilon_0\epsilon A} \end{aligned} \quad [5.17]$$

The two coefficients  $A_1$  and  $A_2$  contain information about the fibre properties. The term  $A_1$  [ $m^{-1}$ ] is related to the initial charge density of the fibre,  $\sigma_0$  and  $A_2$  [ $kg.mol^{-1}.m^{-1}$ ] is related to the specific fibre surface area accessible to the dye,  $A$ . The volume of the diffuse electric layer in the Gouy–Chapman model may be regarded as the equivalent to the internal volume of the Donnan model and is the product of the fibre surface area accessible to the dye and the thickness of the diffuse electric layer,  $r_D$ .

### 5.3 Kinetics of dyeing

During the dyeing process, dye is transferred from the dyebath to the fibre. The dyeing process includes typically at least three stages, any of



which can control the dyeing speed and also the dyeing result (Jones, 1989, p. 373):

1. Transport of the dye through the dyebath to the fibre surface.
2. Adsorption of the dye molecule at the fibre surface.
3. Diffusion of the dye from the surface to the interior of the fibre.

In some cases, such as azoic, metallisable, vat, sulphur or reactive dyes, the dye molecule additionally reacts with or in the fibre after diffusion, which can be considered a fourth stage. In the case of disperse dyes, also in the case of vat and sulphur dyes, dissolution of the dye particle is a prerequisite step before diffusion can take place. The term 'adsorption' refers to a surface phenomenon. When it is intended to refer either to no specific step of the dyeing process or to all steps simultaneously, the term sorption is preferable.

To provide an explanation of the dyeing process based on physicochemical laws, various models have been developed. Since dyeing is a three or, in the case of some types of dye, a four or five stage process and as each individual stage may limit the dye uptake rate, a mathematical model aiming at simulating all steps of the dye transfer would be a complicated one. It is therefore usually presumed that only one or maybe two of the steps determine the overall speed and the model consequently focuses on these. As transport of dye by diffusion within the fibre is often the slowest of all steps, it is at the centre of many models. When no physicochemical models are available, empirical relationships are often used.

### 5.3.1 Transport from bath to fibre surface

The flow of the dye liquor in a dyeing machine, which is normally generated by a pump, results in a macroscopic speed of the dye molecule on its way to the fibre that may be called convective diffusion (Breuer and Rattee, 1974, p. 105). Immediately at the fabric surface, however, there is no macroscopic flow. Consequently, the liquid speed increases from zero at the fibre surface until it reaches the value of the bulk phase. The area where the speed has not reached that of the bulk phase can be interpreted as a liquid layer, extending from the fabric surface to some distance into the dyebath. This hydrodynamic boundary layer, defined as the area in which the liquid speed is less than 99% of the bulk flow speed, causes in turn a dye concentration gradient. The area of the concentration gradient is sometimes called the diffusional boundary layer and has about one tenth of the thickness of the hydrodynamic boundary layer (McGregor and Peters, 1965).

The last section of the dye molecule's path from the liquid to the fibre surface is therefore confined to diffusion through this liquid layer. Consequently,

the dye uptake rate may be reduced if dyebath agitation is not high enough to transport the dyestuff faster to the fibre surface than the rate at which it is sorbed by the fibre. The influence of the liquor flow rate on the exhaustion rate has been known for a long time (Armfield, 1947) and has been confirmed several times since then (Alexander and Hudson, 1950; Brooks, 1972; Ethers and English, 1988; Vickerstaff, 1954, p. 144).

The effect of the boundary layer on the exhaustion speed can be explained mathematically under certain assumptions. Provided a constant diffusion coefficient, a Langmuir-type or Freundlich-type sorption isotherm and infinite bath, it can be shown that the overall diffusion speed depends on the dimensionless variable  $L$  ( $L$  is introduced in one of the boundary conditions in the solution of Fick's Second Law) (McGregor and Peters, 1965). For a Langmuir isotherm,  $L$  becomes:

$$L = \frac{D_s l}{D_f \delta K} \left( \frac{[D]_{\text{sat}}}{[D]_{\text{sat}} - [D]_{\text{f,eq}}} \right) \quad [5.18]$$

For a Freundlich isotherm ( $n = 0.5$ )  $L$  becomes

$$L = \frac{D_s l}{D_f \delta K^2} ([D]_{\text{f,eq}} + [D]_{\text{f}}) \quad [5.19]$$

The smaller the value of  $L$  is, the more the system is controlled by liquid diffusion, i.e. the higher the influence of the boundary layer on the dye uptake rate. The equations show that  $L$  is reduced by an increase in the boundary layer thickness,  $\delta$ , e.g. due to a lower flow rate. Bulk flow velocity,  $v_0$ , and boundary layer thickness can be quantitatively correlated if the model of a plane sheet immersed in a flow parallel to its axis is employed. In this system, the average boundary layer thickness is (McGregor and Peters, 1965):

$$\bar{\delta} = 1.47 \left( \frac{D_s}{v} \right)^{\frac{1}{3}} \sqrt{\frac{vx}{v_0}} \quad [5.20]$$

Here, the average boundary layer thickness is used because  $\delta$  is a function of  $x$  and  $\delta$  is therefore averaged over  $x$ . Thus, the correlation between  $L$  and  $v_0$  becomes:

$$L \propto \frac{1}{\delta} \propto \sqrt{v_0} \quad [5.21]$$

Doubling the bulk flow velocity therefore would result in a 1.4-fold increase in  $L$ . When the flow is not parallel but perpendicular to the fibre surface, i.e. if the fabric and the liquor flow are at a 90 degree angle to each other, the

boundary layer thickness hardly varies with the velocity of the bulk liquid (Kretschmer, 1990).

Equations [5.20] and [5.21] also show that  $L$  becomes smaller for a high partition coefficient, i.e. high dye substantivity and for a high diffusion coefficient in the fibre. The dyeing process would therefore be more sensitive to changes in the liquor flow rate under high substantivity conditions. Note that the value of  $L$  will usually vary during a dyeing process since neither substantivity nor the diffusion coefficient are constant. For  $L$ -values bigger than ten, the system is for practical purposes determined by film diffusion only. Commercial dyeing machines are estimated to have an  $L$ -value of about 20 and would therefore be little influenced by boundary layer phenomena (Etters, 1994).

The initial model for which the parameter  $L$  was derived applied only to an infinite dyebath, i.e. a dyebath with very high liquor-to-goods ratio so that any change in the dyebath concentration over time is negligibly small. Since then, the model has been extended to cover transitional (initially constant then continuously decreasing dyebath concentration) and finite (continuously decreasing dyebath concentration) dyebaths (Etters, 1991). The model has been shown to be helpful in the explanation of polyester dyeing with disperse dyes (McGregor and Etters, 1979).

Experiments with C.I. Reactive Blue 109 on cotton print cloth could only partially confirm the relationship expressed in Equations [5.20] and [5.21] (Etters and English, 1988). The tests showed, as expected, that a higher agitation rate led to a shorter half-time of dyeing, i.e. the time necessary to achieve 50% of equilibrium sorption. On the other hand, however, changes in dye concentration did not influence significantly the half-time. An explanation forwarded by the authors is that the relatively low values of the partition coefficient obtained for the range of dye and salt concentrations used in the experiments meant high values of  $L$ , indicating that the uptake is film diffusion and not liquid diffusion limited. That would explain why dye systems with higher partition coefficients like acid dyes on wool exhibit a dye uptake rate that may be sensitive to dye concentration.

A similar model was suggested by Gooding *et al.* who concluded from measurements with a channel flow cell, that for certain dyes the rate of adsorption is controlled by a porous surface layer (Gooding *et al.*, 1998). They confirmed that higher flow rates increased the rate of adsorption. They also found that high dye concentrations in the liquid bulk phase block the passage of the dyes through the porous surface layer and reduce the rate of adsorption.

### 5.3.2 Adsorption

There are two types of adsorption: physical adsorption and chemical adsorption. In the case of physical adsorption, or physisorption physical forces' of attraction, such as those of the van der Waals type cause the dye to interact

with the fibre. Chemical adsorption, or chemisorption, is a result of the formation of chemical bonds, which can be of a covalent or ionic nature, between the dye and the fibre. In case of chemisorption, dye molecules are bound more strongly to the fibre surface than in the case of physisorption.

The adsorption of the dye to the fibre surface can be regarded as instantaneous and much faster than the following process of diffusion into the fibre centre (Breuer and Rattee, 1974, p. 87). As a consequence, if the dye-bath turbulence is high enough and if there is no obstruction preventing the dye from reaching the fibre surface, the dye will arrive at the surface more rapidly than it can diffuse into the fibre and will accumulate at the surface. Due to the high speed of the adsorption, the quasi-equilibrium is almost immediately established and differs from the true thermodynamic equilibrium only because the dye continues to diffuse from the surface to the inside of the fibre. The difference between true and quasi-equilibrium can be regarded as small (Vickerstaff, 1954, p. 124). Thus it is not the speed of the adsorption that is of primary interest but the amount of dye adsorption and how it is influenced by various parameters. Since the fibre surface is in quasi-equilibrium with the dye bath, the thermodynamic models of the previous section may be used to approximate the dye amount at the fibre surface. The homogeneity of the adsorption can affect the evenness of dye distribution on the substrate, especially if the dye supply rate varies in a machine near the surface of the material to be dyed.

### 5.3.3 Diffusion

In many cases, the transport of the dye from the fibre surface to the fibre interior, which may be termed film diffusion as opposed to liquid diffusion in the boundary layer, is the slowest, and therefore rate-determining, step of the dyeing process. There are two types of model that scientists have devised to describe diffusion of a dye into a fibre: the Pore-Volume and the Free-Volume model.

The Pore-Volume model assumes that the fibre possesses capillary channels through which the dye in solution travels. The pore model was originally suggested in the 1930s and later extended and further developed by Weisz and co-workers (Weisz and Zollinger, 1968; Weisz *et al.*, 1967). The diffusion in the fibre is several orders of magnitude slower than in water because of the greater mechanical obstruction to movement caused by the fibre and because of the greater physicochemical attractions between fibre and dye. It was shown, however, that the measured diffusion coefficient in the substrate can be converted into a 'real' diffusion coefficient, which is close to the coefficient in water if it is assumed that diffusion takes place only in water-filled pores and that adsorption occurs from the inner surfaces

of these pores. Agreement with the ‘true’ value in water could be further improved when the reduction of effective pore radii posed by the presence of dyes was taken into account (Hori *et al.*, 1982).

In the Free-Volume model, by contrast, the fibre does not have pores. Instead, the dye enters the fibre through openings which are created by random movements of the amorphous polymer segments. Crystalline regions of the fibre polymer are normally assumed to be inaccessible to the dye molecule. The segmental movements and the free-volume increase with temperature and become significant only above the glass-transition temperature of the fibre which means that the amount of dye sorption below the glass-transition temperature is negligibly small (Manabe, 1996, p. 216).

Dye diffusion into cellulose is normally described with the Pore-Volume model. Polyester is a fibre example for which the Free-Volume model may be applied. For acrylic fibres, it has been shown that both models apply simultaneously (Zollinger, 1989).

Modelling of diffusion through a film is usually based on Fick’s Second Law of unsteady state diffusion. Textile fibres are frequently considered to have the shape of a cylinder as a first approximation. The diffusion equation is therefore expressed in cylindrical coordinates. The radial diffusion into a one-dimensional cylinder can be written as:

$$\frac{\partial[D]_f}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( rD \frac{\partial[D]_f}{\partial r} \right) \quad [5.22]$$

where  $D$  is the diffusion coefficient of the dye in the fibre and has the units [ $\text{m}^2 \cdot \text{s}^{-1}$ ]. In order to simplify the analytical solution of model equations, it is often assumed that  $D$  is a constant or only temperature-dependent according to the Arrhenius equation:

$$D = D_0 e^{-\frac{E_A}{RT}} \quad [5.23]$$

In many real systems, however, the diffusion coefficient of a dye within a substrate depends in complex ways upon several variables, such as dye and electrolyte concentration, temperature and substrate properties.

#### 5.3.4 Dye depletion effects

In an industrial, more complex dye–fibre system, there are additional factors which may affect the overall dye uptake rate. One of them is the mechanical accessibility of the fibre to the dye which is heavily influenced by the geometrical arrangement of the fibres within the fabric. In a woven fabric, for example, dye penetration at the yarn intersections may

be inferior for this reason. Compared to individual fibres the dye uptake rate of fabrics can be reduced by this microscopic depletion effect by up to half. The effect decreases with increased dye concentration (Hoffmann, 1989). Interestingly, if the fibre density is further increased, e.g. in yarn packages, the liquor circulation only barely influences the dye uptake rate unless the liquor circulation pump is very weak. This phenomenon is explained by the fact that a slower exhaustion in the surface parts of the package is compensated by an increased exhaustion speed due to the higher concentration in the inner package parts (Hoffmann, 1977, 1989).

A second effect, macroscopic dye depletion due to dye uptake by subsequent layers of fabric or yarn, may additionally contribute to a drop of the dye uptake rate. As the dye liquor travels through the fabric pile or fibre assembly, the dye concentration in the liquor, and as a result also the dye supply to the fibre surface, diminishes. Experiments with acid dyes on wool packages and wool fabrics have shown that microscopic (Brooks, 1972) and macroscopic (Brooks and Nordon, 1971) depletion effects contributed to a drop in the dye uptake rate, whereas boundary layer effects were insignificant.

## 5.4 Dyebath monitoring systems

### 5.4.1 Purpose and principles of operation

Dyebath analysis, i.e. the quantification of dye concentrations in solution by spectroscopic measurements, has helped the scientific understanding of dyeing processes and plays a key role in process optimisation (Carbonell, 1991; Ferus-Comelo *et al.*, 2005). An important reason is, first, that in exhaust dyeing dye unevenness on the substrate and average exhaustion speed of the dyes, the latter can be easily and elegantly measured indirectly by dyebath analysis, are highly correlated (Carbonell *et al.*, 1973; Rüttiger and Ehlert, 1972). This means that the degree of unlevelness, an important quality criterion, can be successfully controlled by adjusting the dye uptake rate to a suitable value. Dyebath analysis is also a useful tool to quantify dye compatibility, another important aspect of process optimisation (Bradbury *et al.*, 1995; Hoffmann, 1988). Third, it is also ideally suited to give indications how the washing-off cycle, a crucial part of the process especially in the case of cotton dyeing with reactive dyes, can be shortened or made more water-efficient (Burkinshaw and Anthoulas, 1996; Hoffmann *et al.*, 1996).

The technology and the history of its development have been reviewed in detail (Ferus-Comelo, 2002; Gilchrist, 1995). The available methods in which

dyebath measurements are used to monitor processes could be categorised upon the following dichotomies:

- On-line (dynamic) versus off-line (static) measurement
- Direct dye liquor measurement versus dye liquor sampling techniques
- Closed-loop control versus open-loop control
- Laboratory scale versus bulk scale
- Reflectance versus transmission measurement
- Continuous dyeing versus batch (exhaust) dyeing.

Dyebath monitoring systems usually employ transmission spectrophotometry but systems based on reflectance spectrophotometry have also been developed (Gilchrist and Nobbs, 1997). For highly concentrated pad liquors as they are used in continuous dyeing, Attenuated Total Reflectance (ATR) is a further option (D'Hulster, 1997).

Depending on the requirements (for example the wavelength range to be measured, stability and intensity of the lamp output), there are different types of light sources, among them tungsten filament and light emitting diodes (LEDs). The dyebath sample is measured in cells made of glass or quartz (the latter are used for measurements at higher temperature and for analysis in the UV region) with a known light pathlength.

The detector, which measures the quantity of light passing through the sample, typically measures the different wavelengths simultaneously with the help of a diffraction grating. As the cell containing the solution without dyes already absorbs, scatters or reflects some light it is necessary to measure the difference between a reference and the sample to be measured. In some instruments, the reference is measured only once at the start and subsequently the samples are measured. Other instruments, for example multi-channel instruments or one-channel instruments with a cell changer, can make a reference measurement before each sample measurement. In the latter case, it is possible to also compensate for instrument drift which increases measurement accuracy. It is the task of the software to convert the signal of the detector, which is proportional to the light intensity, into dye concentrations. This requires a calibration which has to be carried out before the dyeing and during which, similar to the calibration dyeings for a reflectance spectrophotometer, solutions of known dye concentrations are measured. For many dye classes the dyestuff–dyestuff interactions in solution are significantly more pronounced than on a textile substrate. Therefore it is advisable to use mixtures of dyes, rather than a single dye, in the calibration solutions.

## 5.4.2 Measurement challenges

Difficulties in accurately determining the dye concentration in solution arise because of deviations from the Beer–Lambert law, i.e. the dye's extinction coefficient is not constant but varies with process conditions (Gilchrist, 1995). Generally speaking, two types of approach have been developed to overcome these difficulties. The first approach attempts to bring the dye-bath sample to standard conditions before the measurement. This typically includes control of temperature, pH and dye concentration. The second approach aims at directly measuring the concentration in the dyebath. The effects of temperature, pH and dye concentration on the extinction coefficient of the dye have therefore to be predicted and taken into account in the conversion from absorbance to concentration values.

Commercial systems have generally opted for direct dyebath measurements (Carbonell, 1991; DyeControl, 2008; Ferus-Comelo, 2007; Tecnorama, 2009) unless they are designed for pad liquors when dilution of the highly concentrated bath facilitates the measurement (Sedo, 2009). Flow Injection Analysis (FIA) and Sequential Injection Analysis (SIA) are examples of systems standardising a dyebath stream before measurement, employed by researchers at the North Carolina State University, USA (Draper *et al.*, 2001; Lefeber *et al.*, 1994). For bifunctional reactive dyes, buffering of dyebath samples with citric acid has been found to improve accuracy (Santos *et al.*, 2009). Even in the case of dyebath standardisation, dye extinction coefficients typically vary with dye concentration so methods have to be employed that predict their variation in this case, too.

Among the methods that have been used for dyebath analysis are multiple linear regression (MLR) in different forms (Berkstresser *et al.*, 1993; Saus *et al.* 1994), the partial least square (PLS) method (Lefeber *et al.*, 1994) and neural networks (Jasper *et al.*, 1993). Although neural networks have been shown to yield accurate predictions especially in the case of non-linear behaviour, their drawback is that they do not accurately predict outside the range of calibration data. MLR and PLS appear to predict with sufficient accuracy if the significant interaction terms that describe the dyes' mutual effect on their absorbance values are included in the model.

The analysis of colourants which are in pigment form during at least part of the dyeing process, such as disperse, vat or sulphur dyes pose particular problems because particles not only absorb but also stray light. Thus the correlation between incident and transmitted light becomes much more complex, depending on the particle size distribution among other factors. One possibility to overcome this problem is to convert the particles into their soluble form, by adjustment of pH in the case of vat and sulphur dyes (Merritt *et al.*, 2001) and by dissolution in solvent/water mixtures in the case of disperse dyes (Van Delden *et al.*, 1996). Even so, direct dyebath measurements, i.e. systems



measuring the dye in particulate form, have proven successful in measuring disperse dyes under industrial conditions (Ferus-Comelo *et al.*, 2005). An interesting feature of one particular direct dyebath monitoring system is that the transition from pigment to dissolved dye can be monitored on-line during the dyeing process, enabling new insights into the mechanism of dyeing and the functioning of dyebath auxiliaries (Ferus-Comelo, 2008, 2009).

In the special case of monitoring reactive dyes it would be desirable to monitor on-line not only dye exhaustion but also the amount of dye covalently bonded to the fibre. Although it does not seem to be possible currently to measure on-line directly the dye fixed on the fabric, the ratio of non-hydrolysed to hydrolysed dye in the dyebath can be used as an indicator instead. As little hydrolysed dye as possible is desirable and is a prerequisite for high fixation levels. Absorbance measurement, however, normally cannot distinguish between hydrolysed and non-hydrolysed reactive dye in solution. In order to surmount this obstacle, FIA has been coupled with high-performance liquid chromatography (HPLC) (Wallace *et al.*, 1997). In this method, a fraction of the combined dyebath-carrier sample that contained two reactive dyes was injected into the thermo-stabilised HPLC column. The total run time for one sample on the HPLC was around 6 min. Although the experiments were in principle successful, the fact that the whole system becomes complicated and expensive suggests unsuitability for routine operations.

### 5.4.3 Future developments

Practical experience has shown that dyebath monitoring systems provide useful information to troubleshoot and optimise dyeing processes (Bradbury *et al.*, 1995; Carbonell, 1991, Ferus-Comelo *et al.*, 2005). The fact that there are several commercial systems on the market indicates that the technology has matured and is likely to be adopted more widely in the future.

A further increase in market penetration will be made easier if the user of a dyebath monitoring system gets assistance in interpreting the measurement data, ideally in the form of a suggestion for the optimum process. At the moment, most dyebath measurement systems are restricted to monitoring, i.e. they are open loop and merely record the dye concentration(s) in the bath over time. The industrial user, however, would be interested in knowing the optimum temperature and dosing gradients as well as holding times and rinsing cycles. From a process control point of view, closed-loop systems would be an improvement. In a closed-loop system, the process variables are adjusted such that the dye concentration in the bath follows a predefined profile. For continuous dyeing, the aim would be for example to keep the dye concentration in the pad liquor constant. In batch dyeing, the aim would be to exhaust the dye according to a linear, quadratic or exponential profile. Experimental work carried out in research laboratories has

confirmed that it is feasible to employ closed-loop control of dyeing processes (Shamey and Nobbs, 2000; Smith, 2007). Cost and reliability of such equipment will decide whether it will be adopted by industry.

An alternative method to closed-loop control, also with aim of providing the user with an optimised process, is to use the measurement data recorded in open-loop systems and to derive the desired by-process by statistical analysis (Carbonell *et al.*, 1985). One benefit of analysing the measurement data after the end of the process instead of during the process is that measurement errors are more easily detected so that the recommendation is likely to be more robust. On the other hand, it implies that the process must first be analysed in the laboratory (in open-loop mode) before the optimum process can be arrived at.

If the providers of dyebath measurement systems manage to offer reasonably priced, robust equipment reliably suggesting more efficient and productive dyeing processes it is conceivable that process optimisation using this tool will become as routine a procedure as the use of reflectance spectrophotometers for colour measurement of textile samples.

## 5.5 Sources of further information

Vickerstaff's book on the physical chemistry of dyeing continues to be a worthy introduction to the subject (Vickerstaff, 1954) but it is no longer in print. The UK-based Society of Dyers and Colourists (SDC) publishes a book on the theory of dyeing which provides in-depth information for those seeking scientific information (Johnson, 1989). Readers looking for more information on the mathematical aspects of developing and solving diffusion equations are referred to Crank's book (Crank, 1979). Results of new investigations concerning theoretical aspects of dyeing continue to appear sporadically in technical journals such as *Coloration Technology* (Wiley, www.wiley.com), *Textile Research Journal* (Sage, www.trj.sagepub.com) and *Dyes and Pigments* (Elsevier, www.elsevier.com).

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## 5.7 Appendix: mathematical symbols

$A$  = Fibre surface area accessible to the dye, [ $\text{m}^2.\text{kg}^{-1}$ ]

$a_f$  = Activity of dye in fibre, [–]

$a_s$  = Activity of dye in solution, [–]

$D$  = Diffusion coefficient of the dye in the fibre, [ $\text{m}^2.\text{s}^{-1}$ ]

$D_0$  = Constant, [ $\text{m}^2.\text{s}^{-1}$ ]

$D_f$  = Diffusion coefficient in the fibre, [ $\text{m}^2.\text{s}^{-1}$ ]

$D_s$  = Diffusion coefficient in the boundary layer, [ $\text{m}^2.\text{s}^{-1}$ ]

$[D]_{f,\text{eq}}$  = Equilibrium dye molality on the fibre, [ $\text{mol}.\text{kg}^{-1}$ ]

$[D]_i$  = Dye concentration in the internal solution of the fibre, [ $\text{mol}.\text{dm}^{-3}$ ]

$[D]_{s,\text{eq}}$  = Equilibrium dye concentration in the bulk solution, [ $\text{mol}.\text{dm}^{-3}$ ]

$[D]_{\text{sat}}$  = Dye saturation molality on the fibre, [ $\text{mol}.\text{kg}^{-1}$ ]

$E_A$  = Activation energy of diffusion, [ $\text{J}.\text{mol}^{-1}$ ]

$l$  = Fibre radius or half-thickness of sheet, [m]

$L$  = Boundary layer variable, [–]

$F$  = Faraday constant, [ $\text{C}.\text{mol}^{-1}$ ]

$\Delta H^0$  = Standard enthalpy of dyeing (heat of dyeing), [ $\text{J}.\text{mol}^{-1}$ ]

$K$  = Equilibrium sorption constant, [–]

$R$  = Gas constant, [ $\text{J}.\text{mol}^{-1}.\text{K}^{-1}$ ]

$r$  = Fibre radius, [m]

$r_D$  = Debye length, [m]

$v_0$  = Bulk flow velocity, [ $\text{m}.\text{s}^{-1}$ ]

$x$  = Length of plate in the direction of flow, [m]

$T$  = Temperature, [K]

$z$  = Number of charges on the dye anion, [–]

$\delta$  = Diffusional boundary layer thickness, [m]

$\bar{\delta}$  = Average diffusional boundary layer thickness, [m]

$\epsilon$  = Vacuum permittivity, [ $\text{C}^2.\text{J}^{-1}.\text{m}^{-1}$ ]

$\epsilon_r$  = Relative permittivity or dielectric constant of water, [–]

$\lambda$  = Donnan coefficient of distribution, [–]

$\Delta\mu^0$  = Standard affinity, [ $\text{J}.\text{mol}^{-1}$ ]

$\mu_f$  = Chemical potential of a dye molecule within the fibre, [ $\text{J}.\text{mol}^{-1}$ ]

$\mu_s$  = Chemical potential of a dye molecule within the solution, [ $\text{J}.\text{mol}^{-1}$ ]

$\nu$  = Kinematic viscosity of water, [ $\text{m}^2.\text{s}^{-1}$ ]

$\sigma$  = Charge density of the fibre surface, [ $\text{C}.\text{m}^{-2}$ ]

$\sigma_0$  = Initial charge density of the fibre surface, [ $\text{C}.\text{m}^{-2}$ ]

$\Psi_0$  = Electrical potential difference, [V]

## An overview of dye fastness testing

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**Abstract:** Colouration does not aim at producing only well levelled shades, the fastness of the dyed textile must be adequate enough for its effective end use. Coloured apparels are subject to various influencing factors that can cause decomposition, sublimation, decolourisation or stripping of colour in selective cases, the final effect of which is fading of the coloured garment. If the colour in the garment is prone to be solubilised or stripped out by detergents, any adjacent white or coloured garments can be stained badly thus compromising the quality of the whole washing load. This chapter describes various aspects related to the importance of fastness assessment and the tests that ascertain the grading of various fastness criteria of dyed textiles.

**Key words:** fastness, grade, grey scale, light, wash, perspiration, rubbing, chlorine.

### 6.1 Introduction

Various colourants used in textiles are not fast to all the influencing factors they face in the course of their regular use. Exposure to light, heat, intense rubbing or treatment with detergents for washing, results in the progressive fading of colour as well as the staining of adjacent garments in selective cases. This can make a garment unusable due to a change in look and aesthetic value. To what extent a specific dyeing can withstand these influences can be ascertained by conducting fastness tests on that particular garment or fabric as a prerequisite to marketing. It is worth mentioning that most of the factors that influence colour fastness are related to dye chemistry, including the mode of attachment of the dye with the fibre, and once this information is known, it becomes possible to forecast the fastness standard of dyeings.

### 6.2 Overview of dye fastness testing

In some cases the prolonged exposure of coloured fabrics to daylight can cause progressive fading of colour due to the action of light on the dye structure. It is also interesting to note that selected areas which are exposed

the most are liable to fade at a faster rate. In textile finishing, mainly functional finishes are applied at elevated temperature in the post-dyeing stage. Coloured garments must also be able to withstand domestic pressing or ironing. Dye must have adequate thermal stability to pass successfully through finishing or pressing, otherwise fading is bound to occur due to sublimation of a part of the dye in each operation, making the shade progressively lighter. Superior washing performance of dyed textiles is needed to avoid staining of adjacent garments in a washing machine. Coloured swimming costumes face the action of the chlorine that is frequently injected into swimming pools to control the threat of infection; dye used for the colouration of costumes must be resistant to this. The physiological function of perspiration, also known as sweating or transpiration, is to assist in regulating body temperature by increasing heat loss due to evaporation from the skin, particularly at high temperatures and during muscular exercises (McSwiney, 1934). But this perspiration causes discolouration of dyeings in selected areas through solubilisation of a part of the dye during use of the garment. Men carrying out welding face fumes which may cause the destruction of colour on their uniforms if the dye belongs to the azo dye class. Rubbing on coloured fabrics may stain white garments due to the presence of superficial dyes. In short, coloured textiles are liable to face various adverse situations through which they have to pass satisfactorily during their use.

The various dyes possess different chemical as well as physical features and they each have their own limitations. In spite of possessing information about the limitations of various dyes, the dyer may have to apply a specific colour on cost grounds, or it may be that a specific hue cannot be produced with any other dye class on a particular textile. For example, brilliant red, orange and yellow colours are best produced on cotton with insoluble azoic colours for the cheapest cost, but at the expense of poor rubbing fastness. Turquoise blue shades on cotton are produced with reactive dyes but have poor wash fastness. Vat dyes possess all round superior fastness properties but their high cost means that they are not commercially viable for many cost-sensitive applications. Direct dyes are cheaper but can only be applied to non-washable cheaper products due to the risk of washing out the dye if the fabric is to be washed in an alkaline detergent. Basic dyes are also cheap and they can be applied to nylon, wool, silk, etc., but they are not preferred for most applications due to their poor light fastness. Polyester is only dyed with disperse dyes; to prevent the sublimation of dye during high temperature curing, thermo-fixation, etc., the dye must have a high molecular weight. The susceptibility of a few disperse dyes to gas fumes, so called gas fading, is due to the action of ozone or oxides of nitrogen ( $\text{NO}$  and  $\text{NO}_2$ ) or sulphur and this susceptibility needs to be assessed in such an atmosphere (Beloin, 1973; SDC, 1982). Gas fading is faster at higher humidity, especially in the presence of durable press finishes.



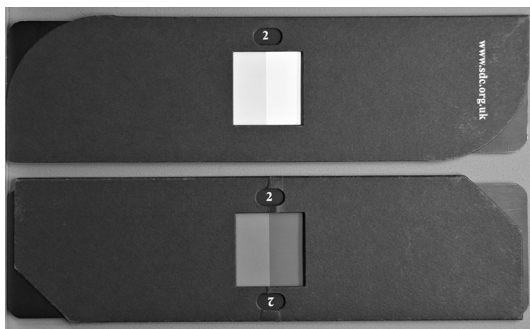
Where the wash fastness of a coloured fabric is unknown, dry-cleaning is usually the most appropriate cleaning method. However, dry-cleaning may also cause fading or a change in colour due to the solubility of colour in solvent and the physical removal of the same by any washing action; the extent of colour change becomes severe for ring or surface dyed textiles (Johnson, 1974).

The assessment of the various fastness properties of dyes in terms of their reaction to light, washing, perspiration, etc., is essential to ascertain the expected performance of the dyed textile in use (Smith, 1994). Technical information provided by various dye manufacturers include reports of fastness testing for individual dyes but this fails to assess the resultant fastness of the dye for a specific dye–fibre combination and when in a mixture with other dyes; as a result dye houses frequently assess the fastness of the dyed products.

### 6.3 Grading of fastness properties

Light fastness is graded from 1 to 8; 1 stands for poor while 8 is for outstanding performance respectively (Pugh and Guthrie, 2001). Eight blue woollen dyed controls of known light fastness from 1 to 8 are used for comparison with the specimen whose fastness is to be assessed. These eight blue woollen controls are produced by dyeing scoured and bleached woollen fabric with blue dyes of known light fastness graded in ascending order as C.I. Acid Blue 104, C.I. Acid Blue 109, C.I. Acid Blue 83, C.I. Acid Blue 121, C.I. Acid Blue 47, C.I. Acid Blue 23, C.I. Soluble Vat Blue 5 and C.I. Soluble Vat Blue 8 respectively.

Other fastness properties are tested by assessing the level of staining of an adjacent white sample alongside the simultaneous fading of the coloured specimen under test. The extent of change in colour (fading) and staining is assessed with two different grey scales graded from 1 to 5 in nine different grades of fading or staining, namely 5, 4–5, 4, 3–4, 3, 2–3, 2, 1–2 and 1, where 1 stands for poor and 5 for excellent colour fastness respectively, e.g. if a dyed sample during a wash fastness test shows no change in colour then there will be no staining of a white sample: the wash fastness will be rated as ‘change in colour –5 and degree of staining –5’ (no change in colour and no staining, i.e. excellent wash fastness) and so on. The look and contrast of grey scales for staining as well as change in colour possessing grades 2 are shown in Fig. 6.1. The same methodology is applicable for all other fastness assessments except light fastness assessment. However, the precision of the result depends on the accuracy and expertise of the evaluator and is also influenced by the viewer’s vision standard as comparisons are made with grey coloured scales (Jaeckel, 1980).



6.1 SDC grey scales to assess staining and change in colour  
(Reproduced by permission of the Society of Dyers and Colourists).

## 6.4 Factors influencing dye fastness

### 6.4.1 Light fastness

Photofading of textile dyes is the most complicated phenomenon relating to colour fastness in fabrics and extensive research is required in order to establish the facts. Light fastness, a crucial property of dyed textiles, is governed by (i) wavelength of incident radiation, (ii) compactness of dye and fibre structures, (iii) dye–fibre system, (iv) degree of dye aggregation and dye particle size, (v) effective humidity (combination of air, surface temperature and relative humidity governing the moisture content on the surface of fibre), (vi) dye induced catalytic action, (vii) temperature, (viii) availability of oxygen (photo-oxidation) or UV light (photo-reduction), (ix) amount of colourant on fibre, i.e. deep or light shades, (x) presence of impurities, namely carriers, dispersing agents, dye-fixing agent, metals and various dilutants, (xi) time of exposure, (xii) exposed surface area under light, (xiii) photoconductivity of dyes and fibres, (xiv) substituent present in dye structure and (xv) stability of aromatic compound. The shorter the incident wavelength, the higher the energy release on the coloured fabric surface and the higher the rate of fading. Anthraquinoid structures (vat dyes) show an excellent light fastness on cotton due to the compactness of the dye structure, which is not possible with other classes of dyes. A more compact fibre obstructs pores and does not allow the passage of oxygen or moisture inside the fabric, thereby suppressing fading. The fact that basic dye produces light-fast shades on acrylic but fails to provide the same on wool, silk, etc., is an example of dye–fibre attachment (Allen, 1987; Bentley *et al.*, 1974). Dyes of bigger sizes generally take more time to initiate fading: fading is inversely proportional to the radius of the dye particle due to the photochemical layer effect (Giles *et al.*, 1977). Effective humidity facilitates the

diffusion of oxygen to the excited dye structure or acts as a highly dielectric reaction medium. In dye induced photofading, vat yellow promotes the fading of blue when in mixture; the latter remains stable if exposed alone. The higher the temperature, the faster the rate of fading; prolonged exposure to visible light causes photo-oxidation depending on the availability of oxygen. The extent of fading over a short time cannot easily be visually assessed in a deep shade, but it will be easier to do so on a light shade because a higher percentage of the dye is destroyed compared to the total in a light shade (Giles *et al.*, 1977; Stevens, 1979). The presence of impurities, some of which are essential to the dyeing process, like carrier, dispersing agent, etc., or metals in the fibre or dye structure, promotes fading. It is a known fact that carriers like *o*-phenylphenol reduce the light fastness of dispersed dyed polyester. The total time of exposure is a vital parameter too; short exposure gives dyed textiles enough time to release energy to go back to their ground state from an excited one. A coarser fibre fades slowly due to the lower surface area to volume ratio, implying that there will be less dye on the surface; the rate of fading will obviously be higher for flat filament and micro fibres. Dyes, while attached to fibres, show *p*-type and *n*-type semi-conductivity and the response time of these should be short; higher light fastness favours higher activation energy for photoconduction (Horton *et al.*, 1976). For improved light fastness, dye must possess a stable aromatic structure with a minimum number of double bonds or reactive substituents (Shakra and Ali, 1995). Electron donating substituents, e.g.  $-\text{OH}$ ,  $-\text{NH}_2$ , etc., accelerate fading while electron accepting groups, e.g. Cl and Br, retard fading (Shakra and Ali, 1992).

#### 6.4.2 Wash fastness

The washing performance of dyed textiles depends on numerous factors, such as dye chemistry, size and solubility of dye, nature of dye–fibre attachment, dye–solvent interaction, location of dye on fibre structure and detergent formulation used in washing.

Reactive dyes are water soluble as well as hydrolysable in the dyebath due to the water–dye interaction. Monochlorotriazine and vinyl sulphone dyes are monofunctional; they attach to the fibre through covalent bonds but also undergo a competing hydrolysis reaction with the water in the dyebath. Thorough washing after dyeing removes hydrolysed dyes completely thus offering excellent wash fastness. This is the reason why these dyes are highly preferred in printing. In contrast, dichlorotriazine reactive dyes form partially hydrolysed dyes and therefore show poor wash fastness. Direct dyes are water soluble and dyeings are never washed unless after-treated; during after-treatment the dye molecule is made larger by reacting with

external chemicals to remain trapped *in situ* on cotton. In the above two cases, especially for deep shades, any loosely attached superficial dye must be thoroughly washed out to ensure acceptable fastness performance.

The opening of polyester's structure in HTHP (high temperature high pressure) dyeing should be adequate to ensure the passage of the dye to the interior of the fibre. Dyeing machines are heated through connecting pipes by injecting steam which is supplied via a boiler. Leakages or condensation in the supply pipe during a typical winter can cause a drop in effective steam pressure. This leads to inadequate opening of the fibre structure well below  $130\pm 2^\circ\text{C}$  and restricts the location of most of the dye to the surface only and results in poor wash fastness during washing.

The final structure of the dye must be big enough to be trapped *in situ* within the fibre. This may be achieved by allowing aggregation of dye. If dyes are insoluble and possess smaller structures, the extent of aggregation will decide washing performance. Better formation of aggregates by anthraquinoid vat dyes promises excellent wash fastness compared to relatively smaller aggregates of sulphur dyes, which show only very good wash fastness. Interestingly in both these cases, the fibre is cotton and the mode of attachment is by means of physical forces.

### 6.4.3 Perspiration fastness

Human perspiration is an emulsion consisting of trace elements, ammonia, urea, amino acid, glucose and chlorides, and the major constituent is lactic acid with a pH of around 6.14–6.57 (McSwiney, 1934). It may be the synergistic combined effect of metal and heat or the emulsion on dye that causes fading of colour at selective points.

### 6.4.4 Rubbing fastness

Rubbing of two different coloured fabrics or one coloured and another white fabric may cause transfer of colour from one to the other. The problem arises mainly from the presence of superficial dyes, which may be due to development of heavy shades, inadequate washing at the end of dyeing, formation of few coloured molecules at the textile–air interface, water solubility of dyes or weak dye–fibre attachment on the surface layer. Wet rubbing fastness tends to produce a lower result when compared to dry rubbing; this may be due to solubilisation of a part of the dye and its migration to the surface of coloured fabric. In forming insoluble azoic colours on cotton, a part of lake is formed at the cotton–air interface where one part of lake remains at the interior of cotton due to padding with naphthol, while the diazotised part remains outside on the surface and the coupling occurs at the interface

imposing a restriction on removal of these lakes during washing causing poor rubbing fastness, an inherent property of naphthol colours.

#### 6.4.5 Chlorine fastness

Colour used to dye or print swimming costumes must be resistant to the action of chlorine which is frequently injected in swimming pools to control the threat of infection. Most of the sulphur dyes and a few reactive dyes are cleaved by chlorine causing decolouration imposing a restriction on these dyes in dyeing costumes.

#### 6.4.6 Thermal stability

The sublimation temperature of a dye must be higher than the temperature that it will go through during curing, finishing, domestic pressing or testing to study migration behaviour; otherwise a part of the dye sublimates off, making the shade lighter. The ability of a dye to withstand high temperature is directly proportional to its molecular weight and intermolecular binding force. For sublimation transfer printing of polyester, for example, the ideal sublimation temperature of selected disperse dyes should be in the range of 180–210°C with corresponding molecular weight of 240–340. Sublimation fastness depends on many factors, such as (i) temperature of exposure, (ii) time of exposure, (iii) shade depth, (iv) chemical structure of the fibre and (v) chemical structure of the dye (Shakra and Ali, 1992).

### 6.5 Application

A list of the fastness assessment for various criteria is too lengthy; only frequently required and conventionally used methods will be summarised here. International organisations for standards prescribe methods to assess fastness grades for greater assessment precision and readers are advised to go through those standards for official endorsement of their test reports with the respective test number.

#### 6.5.1 Light fastness

The comparative study of light fastness on a coloured specimen depends on the basic method of exposing the dyed sample against a selected artificial light source along with eight woollen blue standards. Several attempts were made by researchers to develop an error-free, reproducible colourimetric evaluation to predict light fastness based on Kubelka-Munk function or more precisely its reflectance ( $R$ ). By measuring various colourimetric

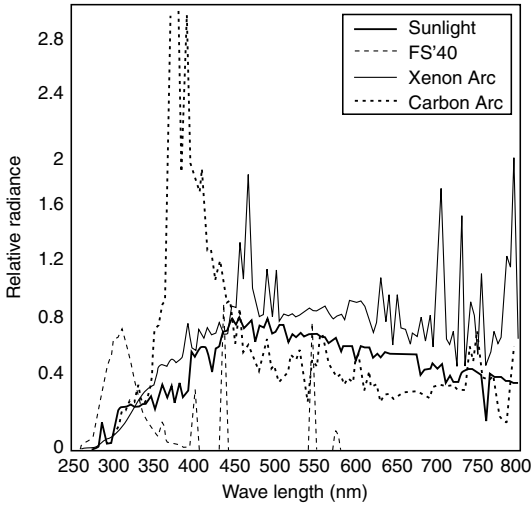
coordinates of the fabric, i.e. colour difference, before and after exposure, it is possible to calculate a rational fastness rating which is more reliable than the classical visual fastness assessment (Burlone, 1982; Convert *et al.*, 1999; Ulshofer, 1986; Vaeck, 1978). Various statistical formulas were also developed, e.g. CIELAB, CMC, SEK, etc. However, such tests hold good for a single dye in a recipe, but a dye in a mixture shade may show catalytic action on the other dyes and complications associated with those cases still motivate people to assess light fastness by visual assessment, which is done by professionals only.

### *Characteristics of various sources of light*

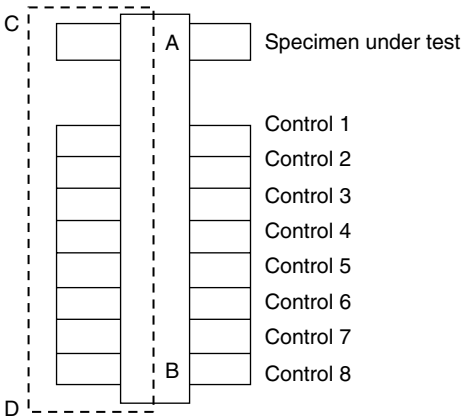
Light fastness of a coloured sample is assessed by exposing it to an appropriate artificial source of light whose energy distribution pattern simulates that of sunlight, e.g. carbon arc, xenon arc, fluorescent sun lamp (FS 40) or mercury tungsten fluorescent (MBTF), together with eight blue dyed woollen control samples of known light fastness grades and is graded by matching with the fading pattern of a specific known control (Friele, 1970; Innegraeve and Langelin, 2002; Pugh and Guthrie, 2001; Sato and Teraj, 1990). The test becomes too lengthy if performed under daylight as the intensity is not consistent. Although various manufacturers of light fastness testers may use a combination of these artificial light sources, from a technical point of view it is the xenon arc that radiates energy with better reliability and in a closer pattern to that given by terrestrial sunlight as analysed in Fig. 6.2 (Atlas, 2009; Park and Smith, 1974). The shorter the wavelength of the selected light source, the higher the energy output and the faster the rate of fading. To get more accurate information of light fastness grades, heat developed on coloured samples is removed by a cooling attachment. Humidity is another important factor, which shows its impact on fastness grades because the test is performed over a considerable length of time.

### *Assessment of light fastness*

Eight known controls and the specimens, 1 cm × 4.5 cm each, are placed side by side on a hinged opaque cover, and the central one-third of each is covered with a black cover AB as demonstrated in Fig. 6.3 (Trotman, 1994). The assembly is exposed to the xenon arc; a heat filter may be placed between sets of samples and the xenon arc to expel UV radiation. Any change in colour in the specimen is inspected by lifting the black cover until the contrast between the covered and exposed positions of the specimen is equivalent to grade 4 on the 'change in colour' grey scale. This is roughly the light fastness rating of the specimen. If control 7 also fades to grade 4 on the same scale, the test may be terminated at this stage. If control 7 does not fade to grade 4, one-half of all controls and the specimen along with half of the



6.2 Spectral energy distribution pattern by various light sources (Courtesy of Atlas Material Testing Technology LLC).



6.3 Arrangement of control and specimen for light fastness test (Trotman, 1994).

central black cover at one side is covered with another black cover CD and is exposed until the contrast throughout between exposed and completely shielded portions becomes equal to grade 3 on the ‘change in colour’ grey scale. The test is terminated at this point.

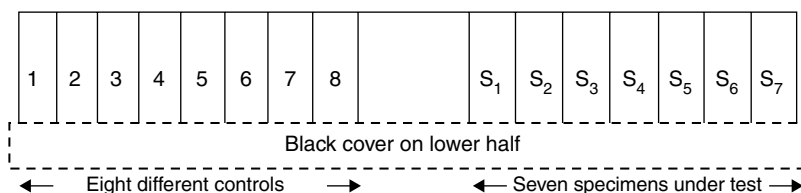
The specimen and the controls now have three clear zones, i.e. a completely shielded area in the middle, a permanently exposed area at the right side of AB and a partially exposed area at the left; the zones are compared with the control and if the two degrees of fading on the specimen do not correspond with the control, the fastness should be the mean of the two.

*Routine checking*

A simple and comprehensive test procedure may be adopted for routine checking. Eight controls of 3 cm × 1 cm size are placed on black paper side by side. Specimens of the same size, which may be large in number and have differential light fastness grades and require simultaneous testing, are also placed at one side of these controls on the same paper (Fig. 6.4). Half of the set is shielded with black paper. The assembly is exposed to the xenon arc. At suitable intervals of time, which depends on the experience of the evaluator, the black cover is lifted and any sort of fading between the exposed and shielded parts of the samples is compared. When control 1 starts fading, the fading of the specimens is checked; if there is no fading until control 1 had completely faded, the light fastness of specimens is considered as above 1. When control 2 starts fading, the same section on the specimen is checked; if there is no fading the evaluator waits until control 3 fades and so on. To confirm the extent of fading at any time, the black cover on the lower half is temporarily removed, the contrast between the exposed and shielded portion is checked and the black cover is reattached in the same position. The light fastness grade of a specimen becomes equal to that of a control, when both of a specific control and one or more specimens start fading simultaneously.

*Assessment without woollen standards*

Light fastness can also be assessed without using blue woollen controls. Incident light on the specimen generates heat, which needs to be removed from the light fastness tester to maintain test conditions, as produced heat shows a synergistic effect enhancing fading. Generated heat is directly proportional to the extent of fading which is added to the effect of incident light (ATIRA, 1996). If the temperature inside the light fastness tester is maintained at  $42 \pm 1^\circ\text{C}$  (the sunlight temperature), the times required for the fading of eight known 1–8 blue controls are 5–6, 10–12, 22–24, 75–80, 155–160, 250–270, 380–400 and beyond 400 h respectively. If the temperature is  $50 \pm 1^\circ\text{C}$ , these values are changed to 3–4, 5–6, 16–18, 50–55, 110–120, 200–210, 325–350 and beyond 350 h respectively. If the temperature inside the light fastness tester differs from these temperatures, the same should be calibrated



6.4 Arrangement of samples for routine test of light fastness.



using eight blue woollen controls. The timings are for a contrast on grey scale 'change in colour' three grade, when the test is terminated. However, the source of light must remain identical to maintain fading with time.

Specimens whose light fastness grades are to be assessed are placed on black sheets as shown earlier with one-half covered. After exposure for the desired time, the cover is lifted, and if no fading is found, specimens are again covered and exposed. A large number of samples can be tested simultaneously using this method without blue woollen controls and the limited life of the lamp can be well utilised.

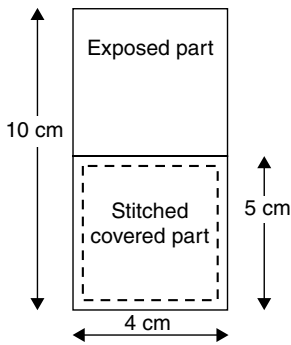
The recently developed software-operated light fastness tester, 'The Megasol Apparatus' by James H Heal and Co reduces complications associated with the use of conventional testers. The Megasol apparatus performs tests through automatic setting and monitoring of test conditions; the instrument sets up and controls the test chamber conditions for up to fifty different standards, sixteen of which are pre-programmed international standards (Heal and Co, 1998). Other rapid and economical testing of light fastness has been detailed elsewhere (Adelman *et al.*, 1977).

## 6.5.2 Wash fastness

There are five test methods to evaluate wash fastness grades which are specifically based on treatment in a laundry soap solution of progressive severity with the addition of alkali and a gradual increase in temperature to keep a match with hand washing to high temperature washing. However, these tests are only laboratory based and, though they have a close match with domestic washings, they fail to meet the demands of customers to have a match with commercial washing practices with varieties of washing detergents across the world (Park, 1975).

One-half of the dyed specimen of 10 cm × 4 cm is covered on both sides with two pieces of undyed outer-lining white fabric (5 cm × 4 cm) made of two different fibres and the three pieces are stitched round the edges, leaving 5 cm × 4 cm exposed as shown in Fig. 6.5 (Trotman, 1994).

For wash fastness test methods 1, 2 and 3, while one of the outer-lining white fabrics is identical in nature with that of the dyed specimen, the type of the second outer-lining is different. If the dyed specimen is made of cotton, silk, linen, wool, viscose, cellulose acetate, nylon, polyester or acrylic, then the second outer-lining white sample will be made of wool, wool, wool, cotton, wool, viscose, (wool or viscose), (wool or cotton) or (wool or cotton) respectively. For tests 4 and 5, one of the outer-lining white fabrics will essentially be made of same fibre as that of the specimen while the second outer-lining depends on the dyed specimen. If the dyed specimen is made of cotton, linen, viscose, cellulose acetate, nylon, polyester or acrylic, the



6.5 Arrangement of specimen for wash fastness test (Trotman, 1994).

second outer-lining white sample will be of viscose, viscose, cotton, viscose, (viscose or cotton), (viscose or cotton) or (viscose or cotton) respectively. Wool has been given undue importance to assess staining in these tests as the second adjacent outer-lining fabric because of its high substantivity for a large number of dye classes. Five sets of composite samples are prepared and treated separately in five different baths with differential chemical formulation and test conditions to assess fastness grades 1–5. Alternately, the first composite sample is tested for staining or change in colour grade 1; on getting a negative result, the second composite sample is treated for grade 2 and so on. After conducting a specific test, the stitches are removed and the three fabric pieces are assessed separately. The exposed portion of the dyed sample is matched with the ‘change in colour’ grey scale to assess the extent of fading, while the white fabric pieces are matched with the ‘change in staining’ grey scale to get the degree of staining; results are expressed as ‘change in colour’ and ‘degree of staining’. Generally these two degrees become identical. Test conditions for five different tests are explained in Table 6.1.

In all these five tests, liquor ratio plays a vital role. The effect of liquor ratio on cross-staining and change in colour, when correlated with the results from laboratory test and those obtained in a domestic washing machine, was found to be that the correlation obtained for cross-staining, but not shade change, is improved when the liquor ratio is reduced below 50:1. A revised setting of 20:1 is recommended for an international ring test to confirm repeatability and reproducibility (Park, 1976; Phillips *et al.*, 2003).

Out of all the five tests described, test 3 is the most important method and the one invariably followed as it has a match with domestic washes conducted with alkaline soap at or around 60°C, especially in tropical summer. All international wash fastness reports are based on ISO-3 test, which is parallel to test 3, if otherwise not mentioned.

**Table 6.1** Parameters of various wash fastness tests

Test number	Chemical formulation	Liquor ratio	Temperature (°C)	Time (min)
1	Soap (5 g/L)	1:50	40 ± 2	30
2	Soap (5 g/L)	1:50	50 ± 2	45
3	Soap (5 g/L) + Na <sub>2</sub> CO <sub>3</sub> (2 g/L)	1:50	60 ± 2	30
4	Soap (5 g/L) + Na <sub>2</sub> CO <sub>3</sub> (2 g/L)	1:50	90 ± 2	30
5	Soap (5 g/L) + Na <sub>2</sub> CO <sub>3</sub> (2 g/L)	1:50	90 ± 2	240

**Table 6.2** Composition of artificial perspiration solutions

	Solution A	Solution B
1-Histidine mono hydrochloric monohydrate	0.5 g	0.5 g
NaCl	5.0 g	5.0 g
Disodium hydrogen orthophosphate	2.5 g	2.2 g
Distilled water	1000 mL	1000 mL
0.1N Sodium hydroxide	Adjust pH to 8	–
0.1N Acetic acid	–	Adjust pH to 5.5

### 6.5.3 Perspiration fastness

Specimen of 10 cm × 4 cm is interleaved between two different specific white unfinished outer-lining fabrics at its one-half (5 cm × 4 cm) as done in wash fastness testing and stitched at the periphery followed by treatment with two different artificial perspiration solutions of acidic and alkaline pH separately; the compositions are shown in Table 6.2 (Trotman, 1994). While one piece of white outer-lining fabric is made of the same fibre as that in the coloured specimen, the second outer-lining white fabric is a different one: if the specimen is made of cotton, wool, silk, linen, viscose, acetate, nylon, polyester or acrylic fibres, the second white outer-lining will be of wool, cotton, cotton, wool, wool, viscose, wool or viscose, wool or cotton and wool or cotton respectively.

The composite samples are thoroughly wetted in two artificial perspiration solutions at liquor ratio 1:50 for 30 min at room temperature and are placed between two glass plates under a weight of 4.5 kg for 4 h at 37 ± 2°C, which is body temperature. Samples are removed from the glass plates, dried at or just below 60°C and change in colour as well as the degree of staining on white are compared and reported (Trotman, 1994).

Alternately, the sandwiched specimen is saturated in the above recipe separately for 30 min at 30°C and kept for 14 h under 4.5 kg weight in a perspirometer.

### 6.5.4 Fastness to chlorinated water

This test is used to assess the resistance of dye in coloured fabric against chlorine which might remain present in swimming baths at low concentrations. To ensure healthy conditions to swimmers, injected chlorine in the swimming pool conditions must be reviewed, details of which are shown in Table 6.3 (Ward, 1983). Eye irritation is substantially reduced if the pH is restricted in the range 7.5–8.0. Only change in colour is assessed and not staining as the costume does not come into contact with a second material in practice.

NaOCl is used as a source of chlorine which, due to its unstable nature, is first titrated to assess the availability of chlorine in it. A standard 1 litre of NaOCl solution is prepared by mixing NaOCl (150g/L available Cl<sub>2</sub>), NaCl (120–170 g/L), NaOH (20 g/L), Na<sub>2</sub>CO<sub>3</sub> (20 g/L). A final test solution of 1.5–2 mg/L active chlorine buffered at pH 7.5–8.0 is prepared from this stock solution. A 10 cm × 4 cm specimen is immersed in the test solution at liquor ratio 1:100 at room temperature for 4 h. It is then rinsed thoroughly with water, dried at room temperature and any change in colour is assessed using grey scale (Trotman, 1994).

### 6.5.5 Rubbing or crock fastness

Testing is conducted using a crock meter which consists of two main parts, that is (i) a rubbing finger consisting of a cylinder of 1.6 cm diameter on which the specimen is mounted tightly with the help of a clamp and (ii) a white unfinished cotton fabric of 5 cm × 5 cm size tightly mounted on another head at the base and just below the cylinder. When started, the cylinder can move up and down in a straight line and tracks a 10 cm path on the white sample at the base with a downward force of 9N causing rubbing. The instrument is run only for 10 s to complete a series of 10 rubs of the movement of the cylinder. Rubbing fastness is assessed by comparing the stained

*Table 6.3* Swimming pool conditions\*

Agitation	Some
pH	7.5–8.0
Temperature (°C)	18–30
Active chlorine:	
–Conc (mg/L)	1.5–2.0, max 3.0
–LR	100 000:1(at 10 m <sup>2</sup> /person)
–Amount(mg Cl/g textile)	150–200

\* Reproduced by permission of SDC.

white sample mounted on the base head with the 'grey scale for assessment of staining' ranging from 1 to 5.

Rubbing fastness is assessed in two ways: (i) dry rubbing and (ii) wet rubbing. In dry rubbing, the white fabric used during testing is dry, while wet rubbing fastness is tested by using a wet white cotton fabric of 100% expression with water.

### 6.5.6 Sublimation fastness

A specimen of 10 cm × 10 cm size is stitched between two specific white outer-lining unfinished fabrics of the same size. While one white outer-lining fabric is made of the same fibre as that of specimen, the second outer-lining white fabric is generally made of polyester. The composite is converted into roll form and placed in a test tube of size 15 mm diameter, the mouth of the tube is tightly closed with cork and is heated at  $120 \pm 2^\circ\text{C}$ ,  $150 \pm 2^\circ\text{C}$ ,  $180 \pm 2^\circ\text{C}$  and  $210 \pm 2^\circ\text{C}$  for 120, 30, 30 and 30 s respectively. At least one of four specimens is prepared for the purpose. The degree of staining of the white adjacent fabrics is reported by comparing with the grey scale for assessing staining for the sublimation fastness at the test temperature and time. Sublimation fastness of pile fabrics is not assessed through this test procedure.

An alternative test method uses a long strip of specimen placed on a sublimation tester; the latter has a few thermostatically controlled heating points at different temperatures (130, 150, 170, 190, 210, 230 and  $250^\circ\text{C}$ ) to heat up the specimen at various points for a specified time and to assess the degree of fading at different temperatures.

### 6.5.7 Fastness to dry-cleaning

The composite sample is prepared as described in the wash fastness test and is treated in  $\text{C}_2\text{HCl}_3$  (trichloroethylene) at liquor ratio 1:100 at room temperature for 30 min with vigorous agitation, squeezed to remove excess solvent, thoroughly washed and dried. The result is expressed as 'change in colour' and 'degree of staining' with the help of respective grey scales. The method stated is for dyed woollen and synthetic textiles.

## 6.6 Conclusions

Assessment of dye fastness is important to maintain quality and forecast the behaviour of coloured textiles against various influencing environments. Not only that, it certainly helps industry to study fastness behaviour of various dye-fibre systems and gives scope for further research on how to

improve these through pre- or post-treatment of dyeings. Though some of the sets of conditions of assessment do not find match with those that occur in practice, these assessments are still of great help in ascertaining the standard of dyeing and their market value. Reproduction of dyed textiles using a different, cheaper class of colour with the same hue and tone may also be examined by evaluating dyeings and the different fastness behaviour of various dye–fibre systems whatever pre- or post-treatment have been imparted to these.

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## Molecular modeling and predicting dye properties

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**Abstract:** This chapter discusses the state-of-the-art molecular modeling methods in the prediction of electronic and thermodynamic properties of organic colorants. The utility of different molecular modeling methods such as Pariser, Parr and Pople (PPP), Zerner's Intermediate Neglect of Differential Overlap (ZINDO) and Time Dependant-Density Functional Theory (TD-DFT) in the prediction of wavelength of maximum absorption ( $\lambda_{\max}$ ), and the effect of crystal packing on  $\lambda_{\max}$  are discussed. Moreover, the prediction of crystal structures using *ab initio* methods and the use of quantitative-structure activity relationship (QSAR) in the prediction of dye-fiber affinity are presented.

**Key words:** molecular modeling, dyestuff, semi-empirical MO methods, *ab initio*,  $\lambda_{\max}$ , DFT, TD-DFT, color, affinity, crystal packing, crystal structure, dye-fiber affinity, QSAR.

### 7.1 Introduction

Over the last two decades, significant attention has been given to the development of molecular modeling methods for accurate prediction of key properties of organic molecules, including molecular geometry, excited state energies, wavelength of maximum absorption, tinctorial strength, heat of formation, entropy, activation energy and susceptibility to nucleophilic, electrophilic and free radical attack.

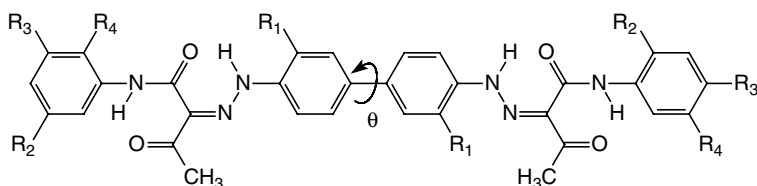
In the case of organic colorants, the ability to model these properties can provide a better understanding of the nature of such colorants at the macroscopic level, and therefore furnish a viable alternative to the development of improved colorants for a variety of applications.

Modeling studies pertaining to organic dyes and pigments have employed: molecular mechanics (MM), molecular dynamics (MD) and quantum mechanics (QM). QM methods have included semi-empirical molecular orbital (SEMO) methods and *ab initio* calculations. Whereas MM has been used to provide standard bond lengths and bond angles, QM has been used to obtain key information regarding geometry, electronic and thermodynamic

properties of various systems. An overview of established QM methods and their suitability for predicting key properties of organic dyes and pigments is presented below.

## 7.2 Prediction of wavelength of maximum absorption

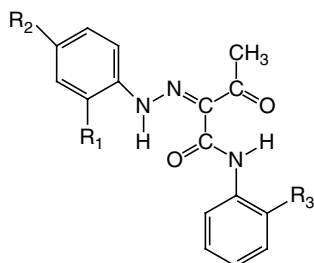
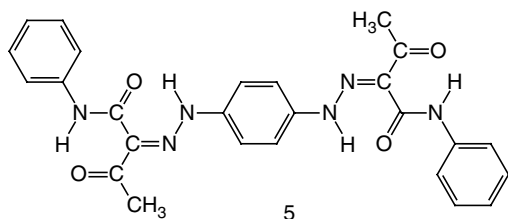
The color of organic colorants is commonly characterized by the wavelength of maximum absorption band in the visible region. The hue, however, is influenced by other electronic absorption and environmental factors,<sup>1</sup> such as shape of the absorption band, band width, intensities, polarization direction and interaction between colorant and solvent molecules (solvatochromism) and aggregation. In the case of pigments, however, studying environmental factors such as solvent effects is difficult due to the inherent insolubility of pigments in the common solvents. Christie *et al.*<sup>2,3</sup> reported good agreement between calculated  $\lambda_{\max}$  values obtained using the Pariser, Parr and Pople (PPP) method,<sup>4,5</sup> after parameterization for the hydrazone tautomer and experimental data for monoarylide and diarylide pigments measured in dimethylformamide (DMF) solution,<sup>2,3</sup> examples of which are shown in Figs. 7.1 and 7.2. A key assumption in this work was that the diarylide pigments (1–4 in Fig. 7.1) adopted a planar structure, which was not the case. X-ray crystal structures showed that the biphenyl linkage has a dihedral angle of  $20^\circ$ .<sup>2,3</sup>



1-4

		R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
<u>1</u>	C.I. Pigment Yellow 12	Cl	H	H	H
<u>2</u>	C.I. Pigment Yellow 83	Cl	OCH <sub>3</sub>	Cl	OCH <sub>3</sub>
<u>3</u>	C.I. Pigment Orange 16	OCH <sub>3</sub>	H	H	H
<u>4</u>	C.I. Pigment Yellow 16	CH <sub>3</sub>	Cl	Cl	H

7.1 Diarylide pigments.



<u>6</u>	Pigment Yellow 1	NO <sub>2</sub>	CH <sub>3</sub>	H
<u>7</u>	Pigment Yellow 74	OCH <sub>3</sub>	NO <sub>2</sub>	OCH <sub>3</sub>

### 7.2 Monoarylide pigments.

Diarylide pigments exhibit higher color intensity than the corresponding monoarylide pigments (6–7 in Fig. 7.2), and it is of considerable importance to predict accurate molar extinction coefficient as well as  $\lambda_{\max}$ . In fact, the high color strength of pigments is a primary reason for their consideration in ink-jet printing.<sup>6</sup> Christie found a satisfactory correlation between the oscillator strength of monoazo and disazo pigments and molar extinction coefficient obtained in DMF solution.<sup>2,3</sup> The oscillator strength (calculated by PPP using Equation 7.1) is the integrated intensities of the absorption band. In this case, increasing the dihedral angle ( $\theta$ ) across the biphenyl linkage, produced a hypsochromic shift and reduction in oscillator strength.

$$f = 4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \epsilon d\nu \quad [7.1]$$

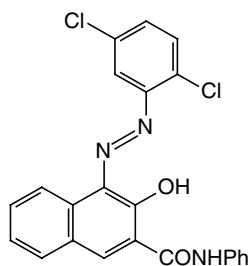
where  $f$  = oscillator strength,  $\nu$  = frequency,  $\epsilon$  = extinction coefficient.

A comprehensive review<sup>1</sup> involving  $\lambda_{\max}$  prediction using PPP reported that the color of organic dyes could be reliably predicted using this method.

It was also shown that the PPP method, when parameterized for a given structure, is effective in predicting the color of the parent compound when different substituents are incorporated.<sup>1</sup> Furthermore, PPP is capable of handling isomers such as azo-hydrazone tautomers.<sup>1</sup> For instance, the PPP method was used to predict the wavelength of maximum absorption of dye tautomers (Fig. 7.3).<sup>1</sup> It is known that the presence of a hydroxyl group *ortho* to azo groups leads to intramolecular hydrogen bonding with the  $\beta$  nitrogen of the azo group, and has a bathochromic effect (Fig. 7.3).

In the same study, PPP was used to predict  $\lambda_{\max}$  and color strength of disazo dyes<sup>1</sup> of the type shown in Fig. 7.4.

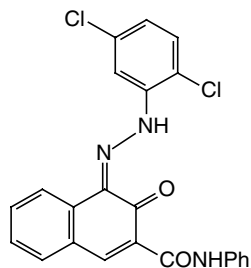
In other studies, PPP was used to study a series of 40 anthraquinone compounds,<sup>7</sup> with a broad range of donor groups. Results indicated that  $\lambda_{\max}$  prediction was poor.<sup>7</sup> In the case of Zerner's Intermediate Neglect of Differential Overlap (ZINDO),  $\lambda_{\max}$  prediction was poor because of incorrect geometry predictions using methods like AM1 and PM3.<sup>7</sup> However, it has been found that the PPP method gives better results due to the consideration of intramolecular hydrogen bonding of the type shown in Fig. 7.5.<sup>1</sup>



8

$$\lambda_{\max}(\text{C}_6\text{H}_{12}) = 425 \text{ nm}$$

$$\lambda_{\max}(\text{calc.}) = 409 \text{ nm}$$

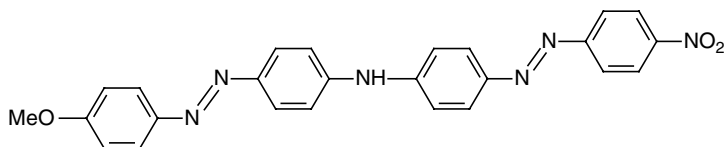


9

$$\lambda_{\max}(\text{C}_6\text{H}_{12}) = 503 \text{ nm}$$

$$\lambda_{\max}(\text{calc.}) = 506 \text{ nm}$$

### 7.3 Azo-hydrazone tautomers.



10

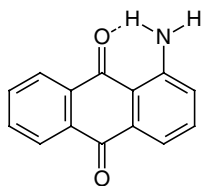
$$\lambda_{\max}(\text{C}_6\text{H}_{12}) = 452 \text{ nm}$$

$$\lambda_{\max}(\text{calcd.}) = 449 \text{ nm}$$

### 7.4 Disazo dye.

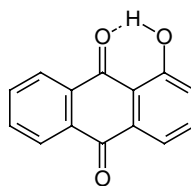
Also the PPP method was used to predict  $\lambda_{\max}$  values for a series of naphthoquinone dyes (Fig. 7.6), giving an excellent agreement with experimental  $\lambda_{\max}$ .

Cyanine dyes are well known for their importance in silver halide photography. An extensive color prediction study using PPP and Complete neglect of Differential Overlap (CNDO) methods<sup>8</sup> showed that PPP was not satisfactory for predicting  $\lambda_{\max}$  values for di- and triarylmethane cyanine-type dyes (Fig. 7.7) using generalized parameters. This could be attributed to: (a) the important solvatochromic effects not accounted for by the method, (b) the fact that the presence of a positive charge on nitrogen gives more  $sp^2$



11

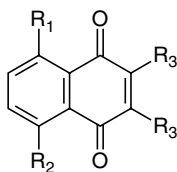
1-aminoanthraquinone



12

1-hydroxyanthraquinone

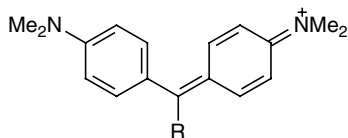
#### 7.5 Intramolecular hydrogen bonding in anthraquinones.



13

$R_1, R_2 = H, NH_2, NHMe, OH, OMe, R_3 = H, Cl, CN$

#### 7.6 A series of naphthoquinone dyes.



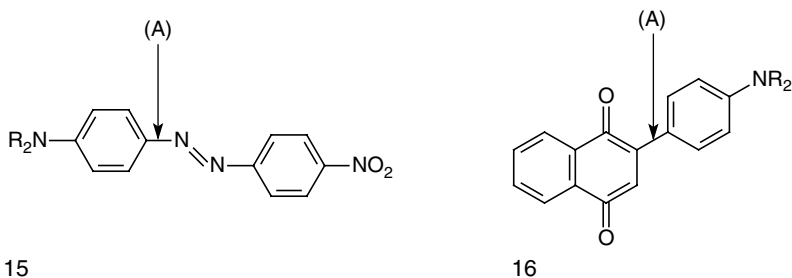
14

$R = H$

$R = Ph$

$R = p\text{-Me}_2\text{N-C}_6\text{H}_4$

#### 7.7 Di- and triarylmethane cyanine-type dyes.

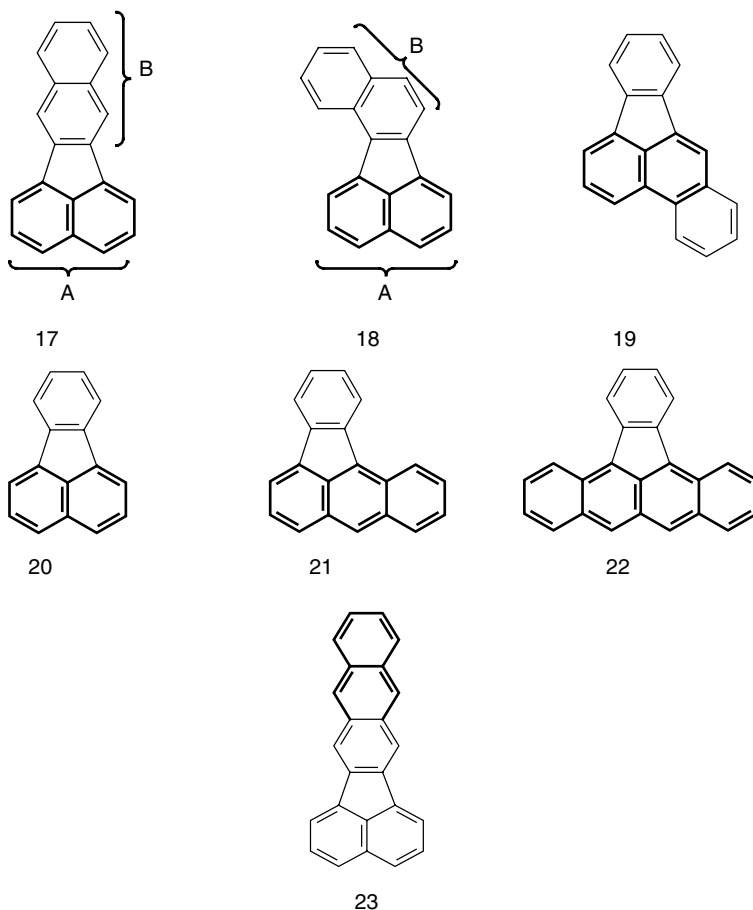


7.8 Precluded coplanarity due to bulky groups in dyes.

hybridization character and (c) PPP assumes coplanarity of which is not the case. Adjusting atom parameters, however, showed a significant improvement in predicted versus experimental  $\lambda_{\max}$  for di- and triarylmethane dyes. In fact, appropriate parameterization of PPP gave effective prediction of  $\lambda_{\max}$  values for indigoid,<sup>9-11</sup> carotenoid,<sup>12</sup> fulvene,<sup>13</sup> cyanovinyl dyes,<sup>14</sup> and fluorescent brightening agents.<sup>15</sup>

Despite the utility of PPP for accurate  $\lambda_{\max}$  prediction of different dye classes, certain significant limitations must be noted. The presence of bulky groups that preclude coplanarity of a dye structure produces hypsochromic shifts due to disrupting  $\pi$ -conjugation of the chromophoric system. Performing PPP, however, after applying bond rotation (e.g. across bond A in Fig. 7.8) via decreasing the value of resonance integral, predicts always a bathochromic shift. However, when a two-center electron repulsion integral was reduced as well the correct hypsochromic shift was observed.

Prediction of bond lengths for polycyclic aromatic hydrocarbons was higher when using the new gamma function. In the case of non-alternate fluoranthrene,<sup>16</sup> PPP was more accurate than *ab initio* calculations. To account for this structure framework, to enhance the effectiveness of the PPP calculations, a spectro-chemical softness (SCS) parameter,  $k$ , was incorporated in the two-electron repulsion integral, new- $\gamma$  (not the conventional  $N-M-\gamma$ ), and this was evaluated based on a spectroactive portion (SP) of the compounds. The SP was determined based on the calculated Molecular Orbital (MO) performed by HMO with reference to *ab initio* MO calculations with 6-31G\* level. Using such modifications provided excellent agreement between experimental and calculated excitation energy calculations of the  $p$ -band (longest absorption band).<sup>17</sup> Some typical examples of non-alternate fluoranthrene are compounds 17–23 in Fig. 7.9 with the SP indicated in bold. The protocol developed<sup>16</sup> to determine SP<sup>17,18</sup> included calculation of both highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) coefficients for compounds 17–23 and comparison with the HOMO and LUMO of naphthalene and



### 7.9 Fluoranthrene compounds.

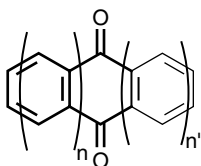
anthracene. Compound 17 maintained the same HOMO and LUMO coefficients as naphthalene does confirming that the SP of 17 is naphthalene. In the case of compound 18, the same HOMO and LUMO coefficients as anthracene was found and therefore the SP of compound 18 is anthracene. The same trend was observed in case of compound 19. The calculated excitation energies for compounds 17–19 using the new- $\gamma$  function were more accurate predictions than those from the conventional N–M- $\gamma$  function.<sup>16–18</sup> In the case of compound 20, however, the HOMO coefficient is maintained in A and B, but only the LUMO coefficient is maintained in A. Therefore, the SP of compound 20 was considered to be A, and the calculated excitation energy produced better results than N–M- $\gamma$  (N–M- $\gamma$ ).<sup>16–18</sup> Similarly, the SP for compounds 21–23 was evaluated using the same approach.

In a separate study, results from calculating the excitation energy of linear *para* acenoquinones (LPAs)<sup>19</sup> (Fig. 7.10) using the PPP new- $\gamma$  function were significantly improved compared to the calculations using the conventional N-M- $\gamma$  function. In this case, the SCS parameter ( $k$ ) for novel two-electron repulsion integrals was accounted for by considering the spectroactive portion of the molecule in question.

### 7.3 Effect of crystal packing on $\lambda_{\max}$

The stability, color and morphology (crystal structure) of dyes and pigments have been studied using MO methods. For instance, three-dimensional molecular stacking behavior and functionalities of aminonaphthoquinones<sup>20</sup> and  $\lambda_{\max}$  values were determined for structures 25 and 26 in Fig. 7.11. Generally, molecular aggregation considerably affects the color<sup>21-23</sup> of the crystal structure and organic non-linear optical properties.<sup>24</sup>

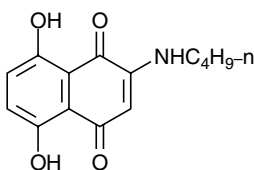
Using PPP, the calculated  $\lambda_{\max}$  of 25 was in good agreement with the experimental value. However, a difference of 100 nm was observed between calculated and experimental  $\lambda_{\max}$  value of 26 in the solid state. It has been shown that the crystal structure of 26 is considerably different from that of 25. X-ray analysis showed that 26 exhibits intermolecular  $\pi$ - $\pi$  interactions<sup>20,25</sup> as well as intermolecular charge transfer dipole-dipole interactions.<sup>20</sup> A four-centered intermolecular charge transfer interaction was observed between the



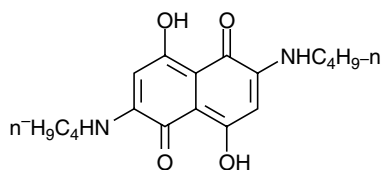
24

Q [ $n, n'$ ]:  $n \geq n'$

#### 7.10 Acenoquinones.



25



26

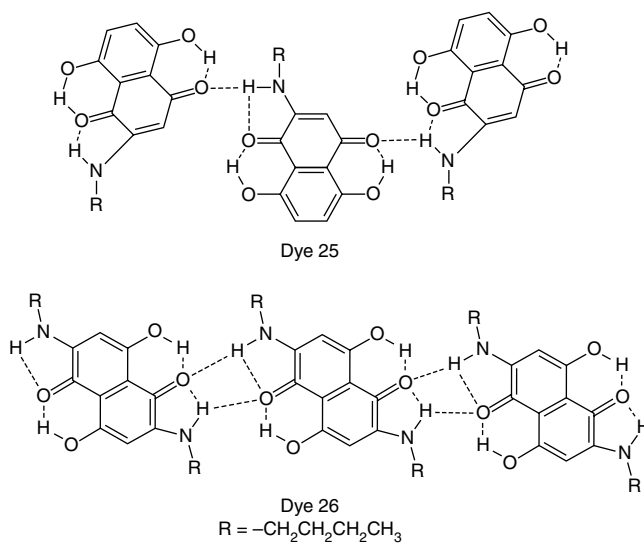
#### 7.11 Aminoaphthoquinones.



molecular layers where the amino and hydroxyl groups function as donors and the carbonyl of the quinone function as acceptors. The distance between the molecular layer was found to be  $\sim 3.33 \text{ \AA}$ , which is the sum of the van der Waals radius for the atoms. The discrepancy between predicted and measured  $\lambda_{\text{max}}$  in the solid state is due to the fact that the PPP MO method does not account for molecular interaction of organic molecules. Figure 7.12 shows the nature of intra- and intermolecular hydrogen bonding between structures 25 and 26 based on X-ray crystallographic data.<sup>20</sup>

The Intermediate Neglect of Differential Overlap, parametrized for spectra, including correlation (INDO/S) method was employed to investigate the structure-spectra relationships for some  $N,N'$ -disubstituted 1,4-diaminoanthraquinones.<sup>26</sup> The calculations were performed using the GRINDOL<sup>27</sup> and INDO-SDCI<sup>28</sup> programs, and the calculated  $\lambda_{\text{max}}$  and intensity values were in agreement with experimental data. On the other hand, Modified Neglect of Diatomic Orbitals (MNDO) was not a suitable method for the conformation of the arylamino group in anthraquinone derivatives (Fig. 7.13).

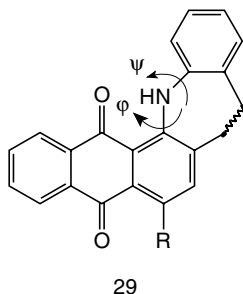
X-ray data for arylanthraquinone shows that the anthraquinone moiety is planar and the N-atom lies essentially in the plane of the anthraquinone and aryl moieties. As depicted in Fig. 7.13, the conformation of an  $N$ -aryl anthraquinones depends on two torsion angles,  $\varphi$  and  $\Psi$ . Reduction in either  $\varphi$  or  $\Psi$  significantly enhances the conjugation between the N-atom lone pair and the  $\pi$ -systems. However, reduction in  $\Psi$  below  $50^\circ$  forces an increase in  $\varphi$  to relieve the steric interaction between the methyl groups in the 2,2'-positions.



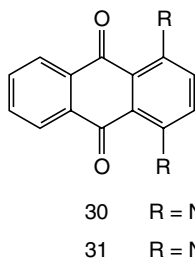
7.12 Intra- and intermolecular hydrogen bonding in structures 25 and 26 (Fig. 7.11).<sup>20</sup>

The results of MO calculations showed that a reduction in  $\varphi$  below  $10^\circ$  while maintaining  $\Psi$  at  $40^\circ$  increased the repulsion energy by  $33.5 \text{ kJmol}^{-1}$ . Therefore, the conformation having  $\varphi = 10^\circ$  and  $\Psi = 40^\circ$  was used as a standard. Excitation energy calculations performed using INDO/S predicted  $\pi-\pi^*$  electronic transitions, corresponding to red and blue absorptions, otherwise known as first and second excited singlet states. Transitions of type  $n-\pi^*$  were not detected due to insignificant changes in oscillator strengths (less than 0.001).

No significant charge was observed between the first excited singlet state for 1,4-diaminoanthraquinone and N,N'-diphenyl derivative (Fig. 7.14). From the second excited singlet state, however, charge transfer involving the N-atom was not localized over the anthraquinone moiety, but rather only on the terminal ring. Hence, the dipole moment of the first excited singlet state was found to be larger than the second excited singlet state, 6.56 and 2.20 D, respectively. INDO/S calculations predicted significant changes in the oscillator strength of these molecules for the first and second singlet transitions, while the transition energies remained unchanged. This was not observed, however, in the case of N-alkyl substituents, demonstrating that the magnitude of the oscillator strength for 29 (Fig. 7.14) arises from interaction between phenyl and anthraquinone  $\pi$ -systems.



7.13 Anthraquinone derivatives.



7.14 Diaminoanthraquinone and N, N'-diphenyl derivative.

In general, PPP and the semi-empirical MO methods CNDO/S and INDO/S do not easily account for changes in  $\lambda_{\max}$  and band intensity due to non-coplanarity in molecules. Recently, however, calculations using time-dependent density functional theory (TD-DFT) were performed on a series of dyes and pigments to predict excitation energy  $\lambda_{\max}$  and oscillator strength.<sup>29</sup> TD-DFT combines DFT with time-dependent formalism, which has been shown to provide increased accuracy in excitation energy prediction.<sup>30–33</sup> TD-DFT has also been effective for both small and large organic molecules.<sup>34,35</sup> Studies involved some typical organic dyes, which are of commercial importance, and compared different basis sets to determine which set provided the greatest agreement with experimental data for each dye class, in terms of maximum absorption and oscillator strength. The dye classes investigated were indigo, azobenzene, phenylamine, hydrazone, anthraquinone, naphthoquinone and cationic triphenyl methane (TPM).<sup>29</sup>

TD-DFT absorption frequency and oscillator strength of the above dyes and its related congeners were calculated using two functional methods as well as three basis sets, namely the hybrid B3LYP and the non-hybrid BPW91,<sup>36</sup> and 6-3G, 6-31G\* (includes a polarization function) and 6-31 + G\* (includes polarization and diffuse functions). The TD-DFT performed was implemented using Gaussian 98.<sup>37</sup> Calculations revealed a significant energy difference between the hybrid and non-hybrid functional. The calculated excitation energies using B3LYP are higher than that of BPW91 ranging from 0.2 to 0.56 eV. However, excitation energies using non-hybrid BPW91 and BP86 functions were in close agreement. The same trend was observed with hybrid B3LYP and B3PW91 functionals. However, the highest correlation with the experimental data was obtained using B3LYP. Also, it was found that a combination of B3LYP and 6-31G yielded the highest overall correlation best results of all basis sets and functional employed in the study. The mean difference in excitation energy between experimental and calculated using TD-DFT is 0.19 eV (38 nm) compared to 0.48 eV (75 nm) using INDO/S. However, it was reported that the difference in excitation energy of the calculated values using TD-DFT and experimental were less than 0.40 eV except in case of cationic dyes, azobenzene and hydrazone dyes.<sup>29</sup>

Based upon the calculated and experimental values of the different dye classes studied, it was assumed that the dyes adopted a limited number of nuclear conformations (i.e. the dye structure did not change during the transition; such cases include naphthoquinone, indigo, anthraquinone and phenylamine based dyes). However, changes in nuclear conformation increase the chance of predicting the wrong geometry in the excited state as it might considerably differ from its geometry in the ground state. Predicting the wrong dye geometry in the excited state produces significant difference between the calculated and the experimental  $\lambda_{\max}$  value of

the dye under investigation.<sup>29</sup> Moreover, dye molecules may adopt different conformations in solution which significantly affects the degree of aromatic stability of the dye.<sup>29</sup> Such perturbation in the aromatic stability produced from the solvent environment commonly produces a significant shift in the  $\lambda_{\max}$  (solvatochromism), which can only be predicted if the solvent effect is accounted for either implicitly or continuously.

A recent study using *ab initio* calculations successfully modeled the effect of solvent environments on the azo-hydrazo (*A-H*) tautomerism of phenylazonaphthols.<sup>38</sup> Using a newly developed spectroscopic method, the tautomeric ratio defined as  $k_T = [H]/[A]$  increases in the order, *iso*-octane < DMF = ethanol < DMSO < methanol = ethyl acetate = acetone < acetonitrile < 50% ethanol/water < CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> = formamide < water. However, in the case of 1-phenylazo-2-naphthol and 2-phenylazo-1-naphthol, solvatochromism is not strong due to intramolecular hydrogen bonding stabilization.<sup>39,40</sup> The absence of intramolecular hydrogen bonding in 1-phenylazo-4-naphthol made this class of compounds ideal for studying solvatochromism via *ab initio* methods. Using Gaussian 94, the effect of polarity on  $\lambda_{\max}$  effect of the dyes was modeled by defining the dielectric constant of the solvent. It was assumed that the solvent produces a continuous environment of uniform dielectric constant in which the only dipole interaction is between the solvent and dye. Using this method, no correlation was observed between the energy gap of *A-H* and tautomeric constants in different solvents, indicating that the interaction between the dye and solvent is specific. Therefore, another (explicit) approach was employed, which specifies the addition of solvent molecules at specific dye sites in which interaction is plausible.

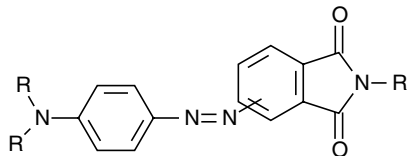
In both *A* and *H* tautomers, the interaction sites are of course different because of the proton exchange. It was found that in the case of water as a solvent, the hydrazone form is more stable due to interaction of water with NH on the dye. In the case of CH<sub>2</sub>Cl<sub>2</sub>, the hydrazo (*H*) form also was more stable although methanol azo tautomer was dominant. These predictions were in complete agreement with experimental data thus substantiating the explicit approach. The *ab initio* calculations employed in this study was at HF/6-31G\*\* level. In essence, from the calculations performed and experimental results obtained the primary factor influencing the tautomeric constant of azo-hydrazone tautomers can be described as: (a) ability of the solvent to form intermolecular hydrogen bonding with a particular tautomer and (b) solvent-solute dipole-dipole interactions.

Griffiths *et al.* showed that PPP could be utilized in predicting the halochromism (protonation) of 4-aminoazobenzene. The extent of halochromism primarily depends on the type and position of substituent groups. Protonation of dye molecule is undesirable for most applications, such as textile dyeing. Therefore, successful prediction of halochromism is desirable. In a separate study,<sup>41,42</sup> positions of maximum absorption ( $\lambda_{\max}$ ) of a series of

phthalimide derivatives were calculated using PPP (Fig. 7.15). It was found that PPP correctly predicted the halochromic effect of the azo phthalimide even in non-polar solvents. One important effect that should be considered prior to modeling halochromism is the level of solvatochromic effect of the dye under investigation.

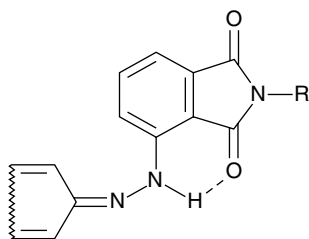
The  $\lambda_{\max}$  value of phthalimide changes upon changing the substituents ( $R$ ) in the imide residue. Also, the formation of intermolecular hydrogen bonding is of considerable importance in this category of compounds (Fig. 7.16). Another factor which can influence  $\lambda_{\max}$  of phthalimide derivatives is imide-iminol tautomerism<sup>43-45</sup> and the conformations<sup>43,46-50</sup> shown in Fig. 7.17.

In a recent study conducted on four solvent-sensitive dyes,<sup>51</sup> the solvatochromic shifts were studied for both absorption and emission bands in different solvents using density functional vertical self-consistent reaction field (VSCRf) solvation model, incorporated with conductor like screening model (COSMO) and self-consistent reaction field (SCRf). The dyes selected have features that likely impact the solvent-sensitive fluorescence of 'push-pull'. These dyes were S-TBA merocyanine, Abdel-Halim's merocyanine, rigidified aminocoumarin (C153) and Nile Red.<sup>51</sup> Both red and blue shifts were correctly predicted and were in good agreement with the experimental observations. Furthermore, it has been shown that incorporating explicit H-bonding between the solute and polar solvent affords the



- 32 R = Me, Et  
 33 R<sup>1</sup> = H, Me  
 34 X = H, NO<sub>2</sub>

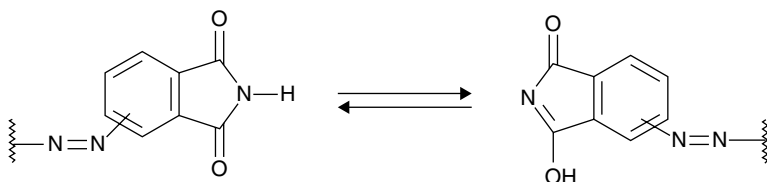
7.15 Phthalimide derivatives.



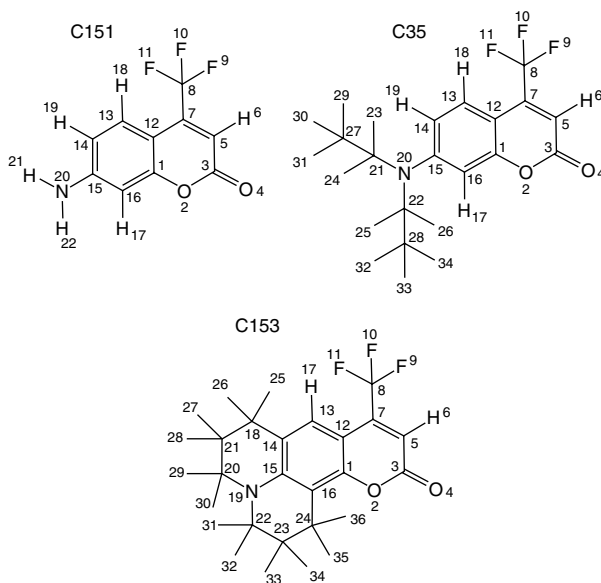
7.16 Intramolecular hydrogen bonding in phthalimides.

correct order of excitation and emission energies,<sup>51</sup> which are necessary to account for color changes of a given colorant in different solvent polarities.

Aminocoumarins are considered an important class of organic compounds owing to their biological activity<sup>52</sup> and absorption in the visible region (350–500 nm), which makes them unique for use as laser dye and non-linear optical<sup>53</sup> chromophore. Hence better and thorough understanding of spectral properties of coumarins is of significant importance in designing more efficient molecules for use as fluorescent probes.<sup>54</sup> Coumarins are known for their strong solvatochromism resulting from a considerable increase in the dipole moment when going from the ground to the excited state, which produces red shift in both the absorption and fluorescence spectra, which is a function of solvent polarity.<sup>55</sup> In a recent study, a hybrid TD-DFT/MM method was used to predict a series of coumarins (Fig. 7.18) in gas phase and solution.<sup>55</sup> The hybrid method provided quantitative information on



7.17 Imide-iminol tautomerism in phthalimides.



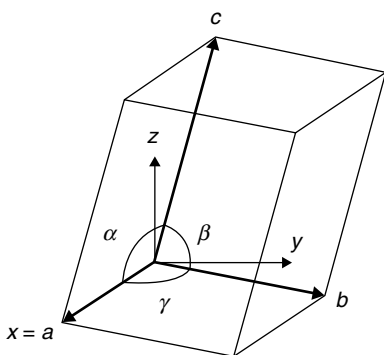
7.18 Aminocoumarins used in DT-DFT/MM hybrid method study.

the red shifts in two different solvent polarities, water and acetonitrile. Further, the method was successful in the prediction of the effects of different N-substituents on the absorption spectra of coumarins.<sup>55</sup>

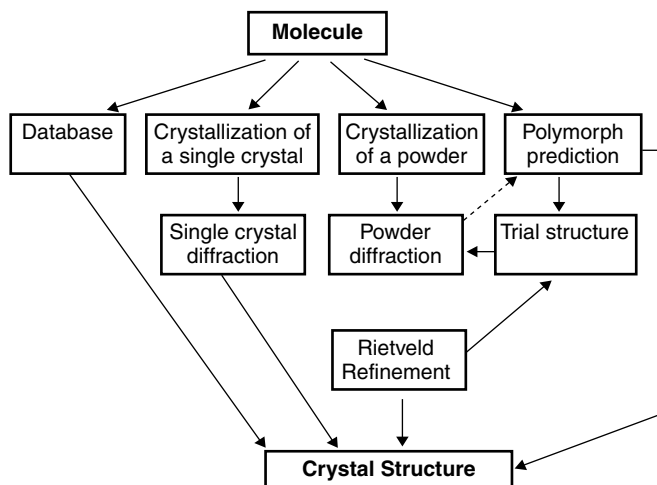
## 7.4 *Ab initio* calculations of crystal structures

A crystal structure is defined by a unit cell, which is characterized by three vectors ( $a$ ,  $b$  and  $c$ ) and three angles ( $\alpha$ ,  $\beta$  and  $\gamma$ ) as shown in Fig. 7.19. Combining the fractional coordinate for each atom of the molecular structure with the cell parameters determines the size and the shape of the crystal structure. Hence, a molecular structure can exhibit different crystal structures depending on how it is arranged in the unit cell. The molecular arrangement to a large degree determines the physical and chemical properties of a compound, including hue, photo- and chemical stability.<sup>56</sup>

The ability to predict crystal structure properties, therefore, is highly desirable, and this is especially true for pigment applications, pharmaceuticals and agrochemicals. Over the last decade, advances in computer power and QM methods for the prediction of molecular geometry, electronic and thermodynamic properties has driven many computational chemists towards the development of protocols to model crystal structures from molecular structural data.<sup>57–62</sup> Crystal structure prediction from the molecular structure without use of experimental data requires *ab initio* models. In the case of pigments, one of the most challenging aspects of crystal modeling is the ability of one molecular structure to exist in different crystal or polymorphic forms. Different polymorphic forms often exhibit different hue, melting points, solubilities, stabilities, etc. Consequently, pigments are often transformed from one polymorph to another thermodynamically to provide improved desired properties. Figure 7.20 shows the possible routes to predict possible polymorphs of a pigment under question.<sup>63</sup>



7.19 Parameters, vectors and the angles defining the unit cell.



7.20 Possible routes of determining crystal structure from molecular structure.

There is a debate as to whether it is possible to predict accurately crystal structure properties. Some researchers have expressed pessimism, such as Gavezzotti,<sup>64</sup> while others believe it is possible only in certain situations.<sup>65-67</sup> Some of the key difficulties in prediction of molecular crystal structure are as follows:

- The calculations are incomplete. Most calculation methods require as input either space group symmetry and the number of independent molecules, or the number of molecules per unit cell. Although the number of space groups is limited, if molecules are distorted an infinite number of packing possibilities will arise.
- Most organic compounds crystallize in different polymorphic forms.
- Often, several minima, with very close energy values, exist which introduce another difficulty in making the decision of which minimum is the correct one.

## 7.5 Quantitative-structure activity relationship in dye-fiber affinity prediction

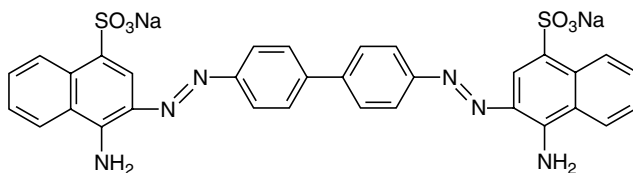
Development of empirical and semi-empirical quantitative-structure activity relationship (QSAR) has potential to provide new insights into, for example, the prediction of dye-fiber affinity and dye-DNA binding. Prediction of dye-fiber affinities is desirable since this is a key property in defining optimum dyeing conditions. Furthermore, measurements of dye-fiber affinities are time consuming. Hence, the ability to predict affinities of candidate dyes



prior to synthesis could enable elimination of a trial and error approach to the design of new dye structures. Similarly, ability to predict with confidence the mutagenicity of dyes would facilitate optimization of the design of environmentally responsible dyes.

The output of QSAR can provide thermodynamic, electronic, solubility and/or steric descriptors. Classical QSAR<sup>68-72</sup> and three-dimensional QSAR<sup>73-76</sup> have been reported for the prediction of dye adsorption onto the cellulosic fibers. Three-dimensional QSAR parameters were derived from the Cartesian coordinates of selected dye molecules. One report stated that electrostatic interaction surpasses steric factors, and polar effects are dominated by hydrogen bonding or dipole interactions.<sup>77</sup> It is well known that binding of a dye molecule to the amorphous region of cellulose is controlled by multiple factors, including electrostatic, and some are thermodynamic. Recently, Woodcock, using MM and a docking technique, reported that the anionic azo dye, Congo Red (Fig. 7.21) is adsorbed on the crystalline region of cellulose surface.<sup>78</sup> Timofei and Walter<sup>77</sup> used PM3<sup>79,80</sup> employed by MOPAC 6.0 package<sup>81,82</sup> to model the adsorption of heterocyclic azo dyes onto cellulose fiber to locate the lowest energy conformation to be used in comparative molecular field analysis (CoMFA) and QSAR descriptors. Of all descriptors used to model dye-fiber affinity, the energies of the HOMO and LUMO molecular orbitals for each dye were the most dominant descriptors. These workers concluded that affinity is associated with a low energy value of the LUMO molecular orbital, and proposed a charge transfer mechanism between the fiber and the dye molecule. Descriptors such as ClogP<sup>77</sup> hydrophobicity showed no correlation with experimental data ( $r = 0.089$ ).

Another study<sup>78</sup> on dye-cellulose interactions involving 27 disperse dyes showed that steric factors are important descriptors for dye-fiber affinity and that hydrophobicity has a negligible effect. A QSAR<sup>83</sup> study involving adsorption of anthraquinone dyes, anionic monoazo dyes, anionic bisazo dyes and disperse dyes adsorption onto cellulosic fiber showed that electrostatic and steric descriptors determine the affinity of the dyes towards the fiber, again more than hydrophobic descriptors. Moreover, the study demonstrated that adsorption of dye molecules onto cellulose fiber increases with increasing positive charge on the dye molecule. The study correctly



35

7.21 Congo Red.

predicted that increased dye adsorption occurs with increasing negative charge on the cellulose surface. The study also showed that dye adsorption increases with increasing conjugation in the dye and that adsorption preferentially occurs along the dye molecular axis. A multi-linear regression (MLR) QSAR study<sup>84</sup> involving 21 disazo anionic dyes showed that electronic and steric effects are the determinant descriptors in defining the binding of a dye to cellulose fiber. A study<sup>74</sup> including CoMFA, semi-empirical (AM1) molecular orbital and multi-conformational minima steric difference (MTD) calculations performed on anthraquinone dyes–cellulose affinity also confirmed that LUMO molecular orbital energy is the most important and contributing descriptor in defining the dye–fiber affinity.

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## Methods and machinery for the dyeing process

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**Abstract:** This chapter discusses methods and machinery for the dyeing of woven fabrics. All common methods of batch or discontinuous, semi-continuous and continuous dyeing are described using examples of the latest production machinery. The dyeing of fabrics, both in open-width form and in rope form is discussed, as are processes involving dyeing under atmospheric conditions and at the high temperatures and pressures required for various dyes. The chapter examines all three types of machines used for dyeing: those in which the fabric is moved; those in which the dyeing liquor is moved and those in which both are moved. Finally, new fabric dyeing technologies are described, along with future developments which will lead to more economically and ecologically viable production processes, addressing concerns about water and energy usage and pollution.

**Key words:** fabric dyeing methods and machinery; fabric in open width or as rope; batch, semi-continuous and continuous dyeing; fabric, liquor or both under motion; emerging technologies; future trends.

### 8.1 Introduction

Textile materials are dyed in various forms including as fibre/dope, yarn, fabric in knitted or woven form, and garments. The dyeing methods and machinery used for each of these forms are specific to the type of material being dyed. The most popular material form for dyeing is woven fabrics; as a result, this chapter will focus on the methods and machinery involved in the dyeing process for this type of material.

The dyeing of woven fabrics is a vast subject since the dyeing machines, dyes and substrates (textile materials) are of substantially different types. Different dyeing machines are used depending on a number of factors, including: dyeing method (batch [discontinuous/exhaust], semi-continuous or continuous dyeing); operating principles (dyebath circulation system, material movement system or system with both dyebath and material in motion) and dyeing conditions (atmospheric conditions, or high temperature [HT] and high pressure [HP] conditions, abbreviated to HTHP).

Textile materials or substrates can be made of a variety of different fibres such as cellulose (cotton, viscose, etc.), polyester, polyamide, elastomer

(e.g. Lycra) and their blends, or can be broadly classified as natural, synthetic or blended. Each type requires specific machines with tailor-made dyeing systems, and these also differ depending on whether the substrate is in open-width or rope form.

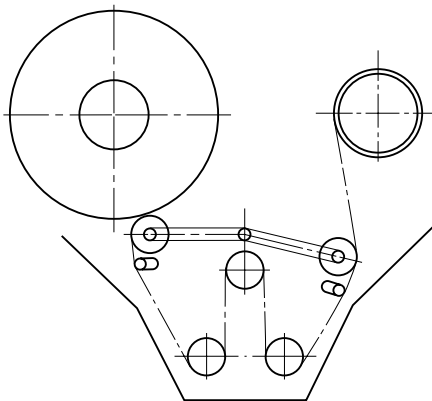
Dyes of different classes (such as direct, reactive, vat, solubilised vat, sulphur, acid, basic, azoic, disperse and pigment) require different machines and methods to ensure their successful application to the textile substrate.

Taking all the above factors into account, a representative sample of the machines currently in use in industrial dyeing and using the latest technology will be presented in this chapter.

## 8.2 Jiggers

### 8.2.1 Dyeing process using a jigger

A jigger or jig is ‘a dyeing machine in which fabric in open width is transferred repeatedly from one roller to another and passes each time through a dyebath of relatively small volume’ (The Textile Institute Manchester, 1975). ‘Full-width piece goods may be dyed in jigs. The cloth is passed from the feed roller through the dyebath, and by means of another roller is given a thorough treatment in the liquor. The treatment in this open vat can be repeated until the desired shade has been obtained’ (*AF Encyclopedia of Textiles*, 1973). Figure 8.1 shows a diagram of a jigger, consisting of ‘a framework, a welded stainless steel box, two take-up rollers, a differential gear, a gear box, a mechanism for automatic change of fabric movement, a counter of passages, straighteners, breaking and threading arrangements and a delivery piler’ (Sadov *et al.*, 1973). The jigger is one of the oldest types of machines used for dyeing woven fabrics up to boiling temperatures. It can



8.1 Diagram of jigger.

dye most types of fabric construction except very delicate and tension-sensitive substrates.

Fabric is wound onto the take-up roller. It is then run through the dye-bath, located in the lower part of the machine, and onto the second main roller. When the roller is fully loaded, the fabric passage is reversed and runs back through the dye bath, before being batched again on the first main roller. The passage of fabric from one main roller to the second main roller is called one turn. The dyeing process consists of a number of such turns. The dye bath trough has a guide roller or rollers at the bottom through which the fabric passes during dyeing while picking up fresh dye liquor. During rotation on the rollers, the dye liquor penetrates and percolates through the fabric facilitating the dyeing action.

### 8.2.2 Developments in jiggers

Jiggers have undergone continuous modifications and improvements over the years to make them more versatile and suitable for use with different fibres and dyes and for a variety of wet processes. There are many 'manufacturers of jiggers, many from India, these being the most common and versatile machines used for dyeing and other related processes in process houses in India. Jiggers can be conventional, semi-automatic or fully automatic. Modern jiggers have electronic controls and their operations could be fully automated. Innovations in these machines include vacuum system and rinse system for effective washing, leading to savings in water up to 75%, higher speeds, very low material to liquor (M:L) ratio of even 1:2, liquor circulation through heat exchangers, energy saving measures, fabric centring devices, automatic sampling stoppage and above all controls in fabric speed and tension to produce uniform dyeing from centre to selvedge and end to end of the batch. With pre-programmable and reproducible dyeing parameters, batch to batch shade variation also is minimised. There are jumbo and superjumbo jiggers for higher production. The most significant development in jiggers is the arrival of the HT dyeing jiggers' (Nair, 2001b, p. 53). The early development of jiggers is described in a number of articles and reviews (Bhagwat, 1994, 1999; Dixit, 1997; Duckworth, 1967–9; Mock, 1997; Wyles, 1984). This chapter will focus on new developments in jiggers that have been made in the last decade, which are also discussed in a number of other articles by the present author (Nair, 1999a, b; Nair, 2001b; Nair and Pandian, 2003a,b; 2005a,b; 2008a).

Of the 27 major jigger manufacturing companies who presented their latest models at Exhibition of International Textile Machinery (ITMA) Paris in 1999, the stand-out company was Mezzera, Italy (now under HTP Unitex Group, Italy), whose many automatic models were shown to meet a number of different requirements. Table 8.1 (Nair, 1999a; Owen, 2002) lists the

*Table 8.1* Features of jiggers of Mezzera (HTP Unitex group), Italy

Models	Area of use	Features
VGC – Metis 300	Production sampling	Smallest; V-design trough; 35 L/m of roller width to give same ratio as in bulk one; direct/indirect heating; hydraulic control for proper fabric tension; two-directional curved bars; double blade of water from spray pipe; bulk conditions simulated.
VGF – Medea 500	Small batches (Normal fabrics)	As above but bigger to dye small production batches
VGSO – Midas 700	Small batches (Light and delicate fabrics – silk viscose, rayons, etc.)	Slightest fabric contact; single perforated trough bottom roller for fabric adhesion (no sliding); minimum tension measures; constant speed and tension; efficient liquor circulation; direct and indirect steam heating
VGO/2 – Milos 800	Small production batches (Delicate fabrics)	Two troughs; high-quality dyeing; tension control by load cells; counter-current washing using two tanks; short liquor ratios; indirect heating; speed adjustments; automated using PLC
VGM – Mars1050	Medium–large batches	As VGF – Medea 500 but for dyeing medium and large batches; low consumption and operating costs; constant speed and tension control by an electronic circuit; uses well-proven oil-driven system of controlled hydraulic motors
VGJ – Mercury 1400	Large-size batches	As above but to dye and bleach large batches; efficient dye liquor circulation; constant speed and tension adjustments; automatic using PLC; direct and indirect heating
VGJ/E-New	Large-size batches	'The best selling Mezzera jigger' (Owen, 2002). New drive system, based on electrical drives and vector-type inverters; closed loop tension control arrangement, using load cells to process even two-way stretch fabrics; electronic control system for automatic operation, programming and storing of data via a PC; vat configuration for lower liquor ratios; jumbo-size batches up to diameter of 1400 mm; roller widths from 1800 to 3800 mm
VGJ/2– Memphis 1350	Production	Versatile production with high technology; counter-current washing using two tanks; intermediate squeezing; oil-driven system of controlled hydraulic motors; PLC automation
Quicker 1350	Production revolutionised	A jigger, dye padder and a small washing line – all in one; vectorial inverter control of speed and torque, tension control by load cells, complete automatic control of processes and functions

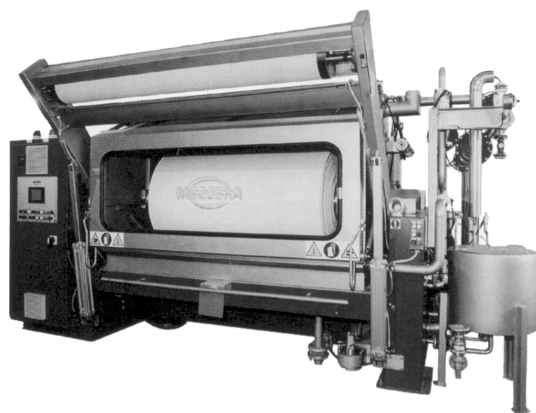
Source: Adapted from Nair (1999a); Anon (2000); Owen (2002).



salient features of Mezzera jiggers. One model is suitable for production sampling and three models are appropriate for small production batches of delicate, light and normal fabrics; these have a number of features that ensure both quality dyeing and fabric protection. Of these models, VGO/2-Milos 800 offers state-of-the-art technology for treating delicate fabrics. Alongside its excellent tension control and speed control measures, it has two troughs, which allow it to achieve:

- short liquor ratios
- drastic reduction in water consumption through counter-current flow
- low steam consumption
- low overall processing times.

There is one model for medium to large batches, two for large-size batches and a further model for regular production. The VGJ/E model has more novel features (Owen, 2002) (Fig. 8.2). Mezzera has brought out Quicker 1350, a new generation machine for discontinuous fabric dyeing, which is a jigger, dye padder and a small washing line in one. Thus, this machine brings together in a single unit all the basic dyeing procedures that up until now have required multiple machines. The introduction of a double trough and the use of a dye padder as a squeezing mangle with an even pressure along the whole length of the nip will lead to high quality processing. All the benefits of the two-trough system, as detailed under VGO/2-Milos 800, will also be available for this model. The squeezing mangle removes about 40% of the water content from the fabric, adding to the machine's versatility. The advanced technology used in this discontinuous machine allows Quicker 1350 to run batches from 70 to 1000 kg while maintaining all parameters to give perfect dyeing uniformity. This machine can carry out and control



8.2 VGJ/E jigger (Mezzera).

pad-jigger processes using various classes of dyes, the fixation process, and the chemical reactions involved during dyeing.

Table 8.2 (Nair and Pandian, 2008a) gives a list of the various types of dyeing jiggers split into three categories: ordinary and semi-automatic; electronic and fully automatic and HT jiggers.

*Table 8.2* Types of jiggers and manufacturers

S. No.	Jigger type	Manufacturers	Models
1	Ordinary and semi-automatic jiggers	Embee (India) Harish (India) HTP Mezzera (Italy)  MCS (Italy)  Swastik (India) Yamuna (India)	Dyeing Jigger Pacific Jigger Mid Jigger VGF-Medea 500 VGSO-Midas 700 Closed Jigger JLN (750 and 1000) Eco-700 and Eco-1000 Jigger
2	Electronic and fully automatic jiggers	Dhall (India) Goller (Germany) Harish (India) Henriksen (Netherlands) HTP Mezzera (Italy)  Küsterns Calico (Germany-India) Lababidico (Syria) Memnon (Turkey) Metal Working (Brazil) Otto-Pricken (Germany) Swastik (India) TEPA (Spain)  Thies (Germany) TVE-Escale (Spain)	Automatic Dyeing Jigger Jigger 2000/Multima Pacific Jigger Atmospheric Jigger VGJ 1400E VGO/2-Milos 800 Quicker 1350 line Calico Hydraulic Jigger Jigger MSD-5550 & MSD-5555 Jigger LT Vario Line Jigger Maxi Jig Electronic Hydraulic Atmospheric Jiggers: JHT-600; JHT-800; JHT-1100; JHT-1250; JHT-1500 Electrical Atmospheric Jigger: JTE-1100 NT-Jigger Jig-Tronic 1100
3	High temperature or HT jiggers	Henriksen (Netherlands) HTP Mezzera (Italy) MCS (Italy) Otto Funke (Germany) Tekst Makina (Turkey) TEPA (Spain)  Thies (Germany)	High-Temperature Jigger Celsius 143 HT Jigger Funke E-Jig Tekst Jigger JHTP-1050 High-Pressure Jigger HT-Jigger

*Source:* Adapted from Nair and Pandian (2008a).

Machines in the third category, HT jiggers, represent the latest developments and have the following general features:

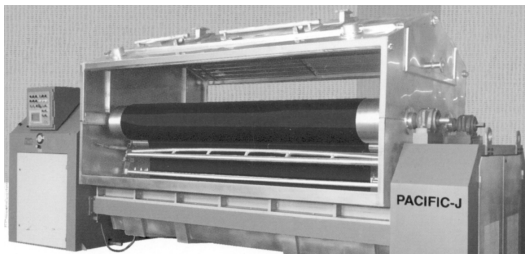
- Closed jiggers (autoclaves) under HTHP for dyeing polyester and polyester blends;
- Fabric in open width as in beam dyeing;
- Fabric in motion as in jet dyeing;
- Dyeing temperatures up to 140–143°C; drip-free hood;
- Liquor ratios as low as 1:2;
- Large fabric batches up to 1500 kg/7000 m;
- Selvedge displacing system to offset selvedge built-up;
- Swing levers for crease-free dyeing even for delicate fabrics;
- Fine fabric tensioning with load cells;
- Speeds as high as 150–200 m/min; variable;
- In and out liquor circulation with pump and butterfly valve controlled flow rate;
- External heat/cool exchanger for faster heating/cooling;
- Fully automatic – Personal Computer (PC) and Programme Logic Controller (PLC).

The features of some recently developed jiggers of various types are as follows (Nair and Pandian, 2008a):

*Pacific Jigger of Harish, India*

Figure 8.3 shows this computerized dyeing jigger with the following features:

- Hydraulic drive with a cushioned start/slow stop;
- Tension adjustment at fingertips;
- Doors fitted with large glass view-ports and with pneumatic lowering and lifting arrangement;
- Steam coils provided in the hood to prevent condensate formation;
- Liquor circulation via a large filtering surface for more even dyeing;



8.3 Pacific jigger (Harish).

- Efficient washing through spray washing above water level;
- Automatic rocking device for avoiding unbalanced batches while the machine is stopped;
- An auxiliary motor for fabric movement under constant tension and also for easy unloading of big batches;
- Continuous level sensor for accurate dosing;
- In fully automatic models, microprocessor controls: temperature, speed, auto-oscillation, dosing, water filling, auto-draining, sampling point, auto-batch-reversing, number of turns and display of process steps;
- Pacific jiggers with Voltage Frequency Drive (VFD) system connected to the power pack can save electric energy by about 25–50% on the installed power and, if required, tension on the fabric can be reduced. For highly tension-sensitive fabrics like silk, customers have the option of choosing the latest generation jigger incorporating load cell and closed loop feedback;
- SCADA (supervisory control and data acquisition) can be installed and networking of multiple jiggers can be carried out to provide: overview of individual machine status viewed on the computer, including current sort number, operator, recipe running and process status; graphical presentation of individual machine; elapsed time and utility consumption, downloadable to any machine in the network; comparison of actual process parameters and recipe parameters; deviation reporting; Management Information System (Service) (MIS) reports; production data per shift; production data per batch;
- Advanced diagnostics to alert operator in case of malfunction and an alarm history for the last 50 stoppages facilitates breakdown analysis.

*Atmospheric Jigger of Henriksen, Netherlands*

The salient features of this jigger according to the manufacturer are as follows:

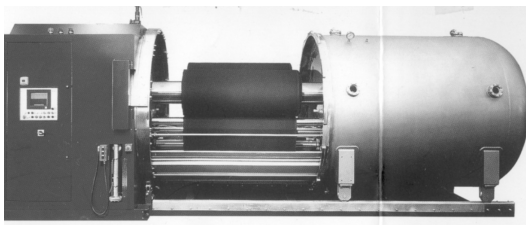
- 'Repro dyeing' systems;
- 'Power rinse' system;
- Automatic water flow-meter;
- AC motors and electronic drives;
- Unique drive algorithm;
- Barco or Setex control interface;
- Pneumatic valves for all functions;
- Liquor circulation system with stainless steel pump;
- Pneumatically lifted doors;
- Steam tight construction;
- Inclined hood preventing drips;

- Additional tank and dosing pump;
- Optional oscillating system;
- Optional batching system;
- Optional centre winder;
- Optional heat exchanger for cooling and for heating;
- Additional chemical valve for completely automated jigger;
- Additional connection for water.

*Celsius 143 of HTP Mezzera, Italy*

Figure 8.4 illustrates this jigger, whose main features are as follows:

- HT dyeing jigger; batch diameter of 220 cm and widening fabric roller from 32 to 115 cm; widths of 180–380 cm;
- Loads up to 1500 kg; suitable to dye synthetics and blends; safe for dyeing up to 143°C;
- Efficient operation; swing levers for crease-free dyeing of even very delicate fabrics; load cells for fine fabric tensioning;
- Drive system with two motors of variable speeds, each controlled by a vector inverter;
- Liquor flow rate control circulation system; trough divided with bulk-head at bottom and two slots for high efficiency counter-flow washing and low M:L ratio;
- Optional addition tanks and automatic dosing system;
- Fully automatic with PLC.



8.4 Celsius 143 (Mezzera).

### 8.3 Beam dyeing machines

Before the advent of jet dyeing machines and HT jiggers, beam dyeing machines were universally used for dyeing polyester and polyester blended fabrics that required higher temperature and pressure. These horizontal fabric beam dyeing machines have proved suitable for dyeing warp-knit fabrics, light-weight woven filament fabrics, polyester blended fabrics

*Table 8.3* Beam dyeing machines

S. No.	Manufacturers	Models
1	Alliance, France	Rotora
2	ATYC, Spain	Superturbo
3	Canlar Makina, Turkey	TECHbeam
4	Dalal, India	Beam Dyeing
5	Dilmenler, Turkey	HT-Beam Dyeing
6	Fong's, Hong Kong-China	CBS HT
7	Hisaka, Japan	LLB Rapid
8	MCS, Italy	Beam Dyeing
9	Minox, Italy	Beam Dyeing
10	Noseda, Italy	New Generation
11	Pozzi, Italy	MAS
12	Tekst Makina, Turkey	TBD Levend
13	Then, Germany	HST
14	Thies, Germany	HT-Beam Dyeing

*Source:* Adapted from Nair and Pandian (2008a).

and so on. In these dyeing machines, the fabric batch remains stationary during dyeing while the dye liquor is circulated through the batch. It is clear from the descriptions of the machines below that many innovations and improvements have been made in these conventional HTHP machines, and these are discussed in several papers and reviews (Bhagwat, 1999; Nair, 1999a, 2001b; Nair and Pandian, 2003a,b, 2005a,b, 2008a; Wyles, 1984). Table 8.3 (Nair and Pandian, 2008a) provides a list of the more popular beam dyeing models and their manufacturers. Of these HTHP machines, Superturbo, developed by ATYC, Spain, has an HP variable pump and 'air-pad' system, and the beam Dyeing Machine developed by Thies, Germany has variable working widths/sizes suitable for dyeing all fabrics in open width including unstructured fabrics. The features of two representative modern beam dyeing machines are given below.

#### *New Generation beam dyeing machines/lines of Noseda, Italy*

The main features of these machines are as follows:

- Full range of process systems available to suit any need.
- Hydraulic circuit for high flexibility for a wide range of applications with woven and knitted fabrics.
- Pumps of AISI 316 ss with high hydraulic and mechanical efficiency.
- New transistor control principle and proper distribution of pressure to reduce the risk of fabric lengthwise movements.

- New beam design with new full/empty ratios to improve flow distribution and to increase centre to selvage and end to end evenness.
- High Production Featured (HPF) models have increased lot size on single beam, improved quality and protection of material, reduced process time and cost with working temperatures of 143–160–170°C.
- Automatic adjustment of capacity/differential pressure, depending on the features of the material processed. Through control of hydraulic parameters, these can work with frequent changes in density during cycles, thereby giving increased process flexibility and reliability along with energy savings.
- Ability to monitor and constantly adjust the specific flow rate and the required number of bath cycles, leading to better quality, economy through optimum use of colours and chemicals and reduction in both process cycle time and production cost.
- Greater reliability and reproducibility of results through the required dosing, such as high and low temperature dosing/linear increased dosing/positive and negative progressive dosing and in-line pH control.
- Volumetric liquor reduction devices that reduce the nominal capacity of single machine to optimise the liquor ratio.
- Axial reduction devices, which help to optimise liquor rates and allow considerable energy savings. Liquor ratio can be adapted to specific needs up to 1–4.
- Functional fittings including: automatic carrier transportation and beam loading, manual and pneumatic beam locking, manual or automatic closing of autoclave and beams adjustable in height without reduction clamps.
- Datawin System to select working parameters and monitor production processes. Its advantages include: guidance to operator in selecting the most suitable working parameters, in calculating ideal and the real capacity values to optimise time/temperature cycles and in calculating real liquor ratio to facilitate production cost control.
- Software package available in a Windows environment version.

*High temperature beam dyeing machine type HST of Then, Germany*

Figure 8.5 shows this compact and versatile machine, suitable for economic dyeing of woven and knitted fabrics in open width. The features of the HST beam dyeing machine are as follows:

- Dyebath circulation by axial-reversible flow pump depending on the type of fabric with reversible liquor flow by heavy-duty centrifugal pump.
- Optimised bath distribution.



8.5 HST Beam dyeing machine (Then).

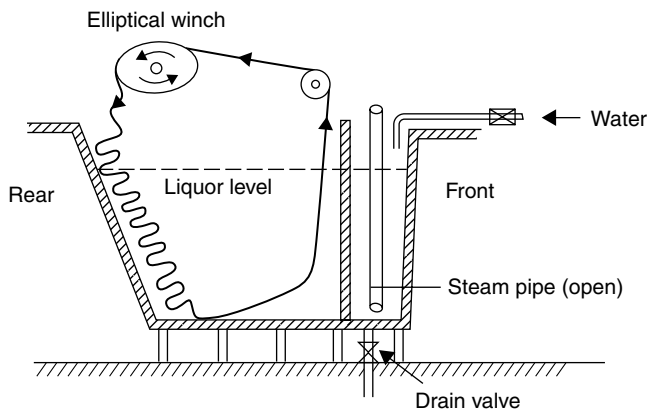
- Equipment includes:
  - (a) Pressure and injection pump with pressure regulation valve and back-cooler.
  - (b) Preparation and expansion tanks.
  - (c) Flow rate controller.
  - (d) Overflow rinse device.
  - (e) Sampling device.
  - (f) Mobile dye beam carrier.
  - (g) Transport trucks for beam carrier with dye beam – possible to use one or more dye beams.
  - (h) Complete switch installation in watertight plastic switch cabinet.
- Machines with semi-automatic control have automatic valves and THEN-Datocomp DCE00 time/temperature controller.
- Machines with fully automatic control are with THEN-Datocomp DCE10 automatic process controller. This can be connected to central host computer THEN-Datocomp DC.

## 8.4 Winches

### 8.4.1 Dyeing process using a winch

The winch is the oldest known simple and low-cost rope dyeing machine with stationary liquor and material moved via a winch reel. This machine exerts only a low tension on the fabric, much lower than that exerted by a jigger, and hence was considered an ideal dyeing machine for delicate and tension-sensitive fabrics such as viscose rayon and the knitted substrates. However, its liquor requirement is greater than the jigger, with an M:L of 1:20–40, resulting in high effluent generation. In this machine, the fabric is in





8.6 Parts and cloth movement in winch dyeing machine.

the form of loops or ropes immersed in the dyebath. The upper part of the rope runs over two reels mounted over the dyebath. There is a smaller reel at the front of the machine above the surface of the dyebath.

The winch consists of a power-driven elliptical reel mounted on a tank that has a perforated partition between a small and a large compartment. The small compartment is at the front of the machine and has a perforated steam pipe, water inlet and outlet. There is a guide roller to move the cloth. Figure 8.6 shows diagram showing parts and cloth movement in winch dyeing machine.

For dyeing, one end of the cloth is passed over the guide roller and then over the winch reel. The machine is then run and the cloth ends sewn together to give a continuous cloth loop. This loop is constantly drawn out of the dyebath and fed into the dyebath from the back to the front of the machine to complete one 'run/circulation' of the fabric in the dyeing process. Solutions of dyes and chemicals are added in the smaller compartment. Due to the movement of the cloth these are mixed well and also move to the rear compartment through the perforated partition. The arrival of modern rope dyeing machines such as jet/softflow/overflow machines has made winch dyeing almost obsolete.

## 8.5 Jet dyeing machines with hydraulic flow system

Of the rope batch dyeing machines, the HTHP jet dyeing machines are the most popular and are widely used for the dyeing of polyester. In these machines, both the fabric and the dye liquor are in motion, thereby facilitating a faster and more uniform dyeing. With the emergence of newer varieties of polyester and polyester blends, these machines have undergone modifications, improvements and innovations to allow them to handle these fabrics.

In rope form, fabrics can be run at higher speeds and in multiple strands for rapid dyeing and higher productivity. Jet nozzles can be of various sizes and shapes to suit different fabric qualities from heavy woven to knits and other delicate materials. Single or multiple nozzle systems exist, as well as combinations of turbo or softflow systems for fabric transport. In terms of capacity, jet dyeing can produce batches of different sizes aided by single tube, coupled and jumbo versions.

The concept of using a jet of dye liquor to transport a fabric rope is credited to Victor Faringer (1958) and the first production machine was exhibited in 1962. Only one machine of this type was presented at ITMA 1967, but rapid progress was made after that, with over 25 jet dyeing machines presented at ITMA 1971 in Paris, leading to the HT winch model falling out of use. A number of papers and reviews have been published that deal with the history and early developments of jet dyeing machines (Nair 1999a, 2001a,c; Nair and Pandian 2005c; 2008b; Peterson, 1973; Ratcliffe 1978; White 1998; Wyles 1984).

Innovations in the design of jet dyeing machines have lowered the required M:L ratio in order to achieve a reduction in water and energy consumption, with the added advantage of limiting the effluent produced. This chapter focuses on these new developments by presenting a selection of the latest jet dyeing machines produced by the world's leading manufacturers.

Table 8.4 (Nair and Pandian, 2008b) gives a list of the leading jet dyeing machine manufacturers and their main machine models, a selection of which are discussed below.

#### *Hi Tech Turbo Jet dyeing machine of Anjani, India*

The main features of this machine are as follows:

- Single tube/double tube dyeing machine with a 'unique design concept, excellent performance and capacity to give 40–45% higher production output as compared to any other conventional make of jet dyeing machine. It gives superb micro depth even dyeing touch with much less energy and chemical consumption, minimum maintenance cost and much less pollution with efficient after sales service network' (Nair and Pandian, 2008b, p. 14).
- Wide angle delivery tube to reduce speed loss and avoid interference of turbulence from dye liquor to achieve faster fabric speed, larger flow volume, shorter process time and higher machine efficiency.
- Lower height difference between tank and delivery tube to reduce fabric tension during running.

Table 8.4 Jet dyeing machines

S. No	Manufacturers	Models
1	ACME, Taiwan	AM-SF Dual Flow
2	AKM, Taiwan	AK-HTO Multiple Flow High Pressure Rapid AK-SL Dualflow High Pressure Rapid AK-BL -do- High Capacity AK-SQ High Pressure Rapid
3	Alkan, Turkey	03C HT Fabric Dyeing
4	Alliance, France	Futura
5	Anjani, India	HiTech Turbo Jet U Type Jet with and without reel
6	Brazzoli, Italy	Innoflow exl Multiflow Must
7	Devrekha, India	User-Friendly Economical Jet Rapid Jet Economical Long Tube Rapid Jet
8	Dilmenler, Turkey	DMS 11HT Jumbo (RDS)
9	Fong's, Hong Kong	ECO-6 ECO-88 Towel-8
10	Hisaka, Japan	Circular-Rapid CUT-SR Type CUT-SRJ Type Jumbo
11	Laip, Italy	205 Jet Rapid New 800 HT New 900 HT
12	MCS, Italy	Multiflow Euro Flow First Vento Universal
13	Minox, Italy	Press Jet Duo flow PRT
14	Obem-Maibo, Italy	Maibo Medusa
15	Proses, Turkey	Eco-Soft Ht Jet Eco-Fast Ht Jet Lycra
16	Sclavos, Greece	Venus
17	Then, Germany	Thenflow Thenjet II
18	Tong Geng, Taiwan	ROL HAF HJF
19	Yamuna, India	HT Jetflow

Source: Adapted from Nair and Pandian (2008b).

- Winch reel of larger diameter offers lower surface tension with the fabric.
- Machine body and wetted parts made of ss 316/316L for corrosion resistance.

- Heavy-duty ss centrifugal pump that provides high flow rate to complement the high fabric speed.
- Reel driven by frequency p.s. controlled motor to achieve speeds up to 600–800 m/min.
- Reversing nozzle that ejects the fabric rope back to automatically release any tangling.
- Highly efficient heat exchanger for fast heating and cooling.
- Colour kitchen with accessories.

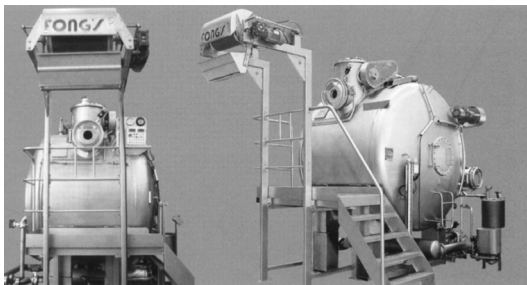
*Rapid Jet dyeing machine of Devrekha, India*

The salient features of this machine are as follows:

- Liquor ratio – 1:5 to (wet fabric);
- Adjustable ball type nozzle;
- Main vessel and basket made of ss 316;
- Motor – 10 HP to 15 HP;
- Fabric drive reel with AC motor and frequency controller;
- HT up to 140°C;
- Working pressure – 4 kg/cm<sup>2</sup>;
- Capacity 25–200 kg;
- Designed with slope on rear construction improves smoother fabric transportation and stable loading condition to get tangle-free operation during the low and HT stages;
- Claimed to be suitable for dyeing delicate materials.

*ECO-6 HT dyeing machine of Fong's, Hong Kong China*

Figure 8.7 shows two views of this latest machine. The main features of this machine are given below:

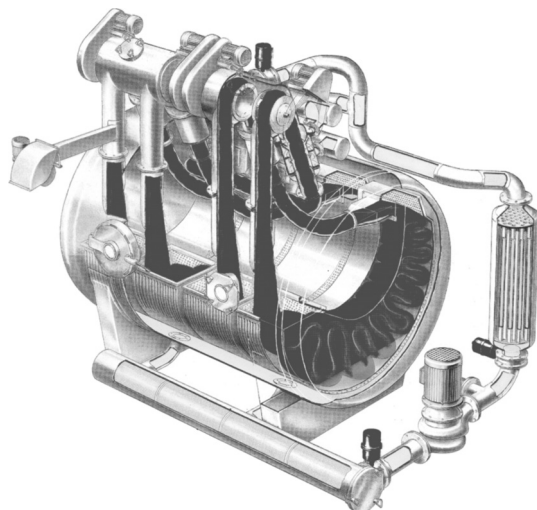


8.7 ECO-6 HT Dyeing Machine (Fong's).

- With its 'well-proven liquid separating and fast circulation technology', it achieves a low liquor ratio of 1:5.
- Its use of advanced polymeric material permits tube capacity up to a maximum 250 kg.
- Its integral design arrangement of the lifter reel, the nozzle and the conveyance tube allows a maximum fabric speed of 350 m/min.
- Maximum working temperature is 140°C with a maximum working pressure of 3.8 bar. It has a heating gradient of 25–100°C at average 5°C/min and 100–130°C at average 2°C/min. This is achieved with dry saturated steam pressure at 7 bar. Its cooling gradient is 130–100°C at average 3°C/min and 100–85°C at average 2°C/min using cooling water at 25°C and 3 bar.
- Its standard features are body and parts wetted by dyeing liquid are made of corrosion-resistant ss 316. Heavy-duty ss centrifugal pump, lifter reel driven by frequency inverter-controlled gear reduction motor, Eco Tech Special (ETS) nozzle, fabric plaiting device for fabric storage chamber, automatic fabric upper-tangling release device, pneumatic control valves for heating, cooling, filling and draining, spray cleaning device, high efficiency tubular heat exchanger, level indicator and controller, service tank with feed pump, valves and stirrer, take off roller, multi-core control cable, seam detector, spare filter insert, service platform, main control cabinet with FC28 microprocessor and dosing control with precision flow control device.
- Its optional extras are multi-saving rinsing system (MSR), multi-intelligent rinsing system (MIR), second service tank, programmable fresh water metering fill, programmable second fill, programmable second drain, layout plaiter, coupling accessories, extra length of multi-core control cable and direct steam heated hot water injection device.
- It claims savings in water, steam, electricity, dyes and chemicals.
- It has accurate programmable metering fill, the optional MSR system with no-drop bath dyeing technique without machine stoppage. MSR results in reduction of process time.
- High shade reproducibility from programmable metering fill, accurate dosing control, programmable nozzle pressure and fabric cycle time control.
- ECO-6 has versions from one tube to eight tubes having nominal capacities from 80 to 3000 kg.

### *Multiflow of MCS, Italy*

Figure 8.8 shows the movement of the rope in this single rope dyeing machine, which is able to dye fabrics with reactive dyes in less than 4 h; thanks to its practical approach to the mechanical and chemical concepts of the phenomenon of dyeing. A single fabric strand runs in a continuous



8.8 Rope movement in Multiflow (MCS).

spiral through the jet nozzles and fabric chambers and then back to the start for repeat runs through the machine. In a four-chamber machine, the movement of the rope in the chambers follows the pattern: 1–4–3–2 and back to 1. The machine has the following features:

- Shorter dyeing cycle (40–60% less) with less time required for loading/unloading, less time needed for addition of dye and chemical additions, and finally less time needed to achieve level dyeing because of the large number of exchanges between liquor and fabric.
- Temperatures of up to 143°C at 3 bar and liquor ratios can be from 1:3 for synthetic articles and up to 1:8–1:10 during washing phases. The maximum revolution speed of the fabric is 450 m/min without causing either rope tension or fabric abrasion by virtue of the appropriately sized inner reels, flow jet nozzles, transport tubes, deposit troughs and fabric/liquor separation and fabric control system in each single section.
- Round-shaped fabric deposit trough suitable for processing both woven and knitted fabrics with different weights and structures; the manufacturers guarantee results in terms of both quality and repeatability.
- Multiflow machine can be equipped with a ‘charge tank’, which will store the next liquid bath to be used in the dyeing machine. This tank can hold preheated water, chemical additions, salt additions, overflow rinse water and recovered liquor.
- Fabric content in each chamber is controlled by PLC and software acting on the inverters for the inner reel drive. The speed of each drive

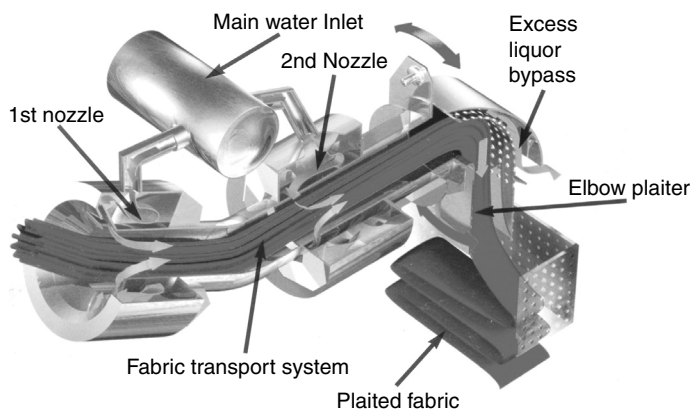
has independent control to ensure equal fabric quantity in each chamber. PLC can be interfaced with any microprocessor for programming and control of any working cycle selected for a particular process and fabric content to maintain the number of liquor/fabric exchanges. These parameters can be memorised for perfect repeatability of the process from batch to batch.

- Compared with the conventional machines, Multiflow claims a 113% larger production capacity. With its high savings in energy cost, the pay-back period is said to be only 9–10 months.

### *Venus of Sclavos, Greece*

Figure 8.9 shows the parts of the Venus fabric rope dyeing machine with ‘twin soft flow’ consisting of two high-flow low-pressure jet nozzles per fabric strand, to provide maximum fabric to liquor interchange. This gentle soft flow action on the fabric facilitates high quality dyeing of a variety of fabrics as a single rope. Its fabric transport system consists of (clockwise in Fig. 8.9): first nozzle, main water inlet, second nozzle, excess liquor bypass, elbow plaiter and the plaited fabric. The important features of this machine are as follows:

- New non-stop ‘thinking’ rinsing system, ‘Aquachron’, which achieves proven savings in water, time and steam. This system can also repeat identical dyeing conditions from batch to batch, ensuring accuracy of shades, and has flexible automation to improve quality and profitability.
- Choice of two ‘Aquachron’ water and time management systems offering control of liquor ratio, cloth speed, strand revolutions, intensive rinsing and liquor level, the controls being adaptable to various cycle control systems:



8.9 Rope movement and parts of Venus (Sclavos).

- The Aquachron ‘Smart’ – the system that memorises and repeats dyeing parameters from batch to batch and independent of the water, steam and energy supplies – ‘a first in reproducibility’;
- The Aquachron ‘xi’ – the ultimate water and time management rinsing system, offering guaranteed performance, high flexibility and the choice of automation depending on the customer needs. This is a productive, fully automated rinsing process without the need for ‘drops and fills’. The intensive cleaning zone of the ‘twin soft flow’ fully maximises the rinsing efficiency while accurately measuring and controlling the flow and temperature of the incoming water. The contaminated water is extracted through a unique liquor bypass which prevents it from coming into contact with the clean fabric.
- Overall results: reduction in consumption of water (55%), steam (46%), power (71%), a drastic reduction in process time (48%) and an increase in productivity (52%).
- Improvements in dyeing efficiency and dyed fabric quality. Up to 50% reduction in shade additions and re-dyeing is also claimed.
- Direct built-in heat recovery system, the first of its kind, which does not require a central installation and offers a constant supply of hot water during the process. This reduces steam consumption and improves productivity thereby leading to additional profits.

## **8.6 Airflow dyeing machines with aerodynamic flow system**

The aerodynamic system for dyeing in these modern airflow or air jet machines makes use of a stream of air or gas for transporting fabric, rather than the stream of liquor used in conventional jet dyeing machines. These machines are therefore also known as air transport dyeing machines, produced both in HT and Atmospheric versions. With the arrival of these novel and revolutionary rope dyeing machines, dyeing has become faster, with improvements in ecology and economy. The M:L ratios have been reduced down to 1:1 and 1:4, almost half or less than half of those of the traditional jet dyeing machines, with savings in water, dyes, chemicals, energy and time. As well as higher productivity, these machines also have higher rope speeds. Dyeing cycles in air jet machines are shorter; dyes and chemicals are injected in an air stream and at the end of the dyeing cycle, the spent dye liquor is drained at HT for faster cooling. Shades are even, uniform and have better fastness properties.

Aerodynamic machines are very useful for dyeing delicate, sensitive and even elastic fabrics made from new generation fibres, mainly for the fashion industry. The shape, design and internal features added to the air transport system guarantee damage-free processing of these new fibre fabrics and

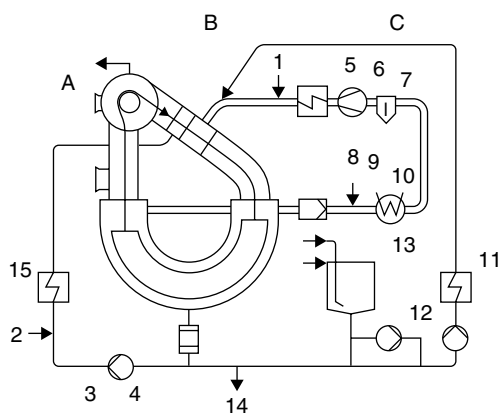


those with surface effects, preserving their smooth and soft surface feel. All types of fabrics – light, heavy, delicate, woven, knitted and with any fibre or blend – can be dyed in these machines, so they are often referred to as universal machines. These machines come in various capacities with one or more chambers. Precise control of all operations, essential for such high speed and advanced dyeing system machines, is carried out electronically, making operation easier. Special control systems, such as DQC (Dynamic Quality Control) for continuous monitoring and DYNET, based on network and remote monitoring of sensors and actuators fitted on machines, have been developed to allow smooth and operator-friendly function. Being universal and offering ecological and economic benefits, these airflow machines appear to be the preferred machines for the present and the future.

Germany is considered a pioneer in this field: it has been reported that the technology behind the aerodynamic system was developed jointly by the German companies Then Maschinen-und Apparatebau GmbH, Schwäbisch Hall and Hoechst AG, Frankfurt/Main (Eltz, 1985).

Figure 8.10 shows the schematic diagram of the layout and circuits of a typical air transport dyeing machine with three circuits, marked as a, b and c in this figure, where ‘A’ stands for liquor circuit, ‘B’ for gas circuit and ‘C’ for injection circuit. The various parts and circuits of the machine are labelled from 1 to 15.

The liquor circuit is designed for dyeing with partially flooded stores. The layout of the aerodynamic system is shown above the gas circuit, with the gas flow being generated by a blower fan. This gas stream, composed of air and steam, emerges from the jet, entrains the cloth and then remains in contact



8.10 Schematic layout and circuits of a typical airjet. A: Liquor circuit; B: gas circuit; C: Injection circuit. 1: Steam; 2: Water; 3: Liquor pump; 4: Liquor filter; 5: Steam/air heater; 6: Blower fan; 7: Trap; 8: Filter; 9: Compressed air; 10: Steam/air cooler; 11: Injection pump; 12: Addition pump; 13: Addition tank; 14: HT discharge; and 15: Heat exchanger.

with it in the following transport zone and in the fabric store. The goods run equally well in both dry and wet states. Dyes and chemicals are injected into the gas stream with the injection pump and dispersed over the cloth. The air and steam are in direct contact with the dyes and chemicals dispersed on the surface of the textile and also with the liquid phase of the liquor dispersed in the gas stream itself. Between these gaseous and liquid media, a mutual exchange of heat and material takes place, the extent of which varies with changes in temperature and pressure. A steam/air heater and a steam/air cooler in the gas circuit provide the optimum temperature for use inside the system, and allow the goods to be dried just after dyeing. Microprocessor controls guarantee proper dyeing results and reproducibility.

As mentioned earlier, in the aerodynamic system, goods are propelled and guided by gas circulation. Higher fabric speeds are feasible with a gas stream than with a hydraulic system, since the fabric is under less tension when it is accelerated. As the textile material is not propelled by the treatment liquor, there are differences in the mode of bath exhaustion. The dyes and chemicals are not taken up from the liquor surrounding the goods but are dispersed on the fabric surface by the gas stream. The liquor ratio is determined primarily by the liquor uptake of the goods.

In these machines, during HT discharge, e.g. at 135°C, the temperature falls rapidly to 100°C due to a reduction in steam pressure from over 2 bar to zero. Evaporation of moisture within the goods prevents crease markings. HT discharge and cooling inside take place in a few minutes as against cooling rate of 1–2°C/min in jet dyeing machines.

The main characteristics of airflow machines are as follows:

- Gas circuit, facilitating:
  - (a) Fixed fabric run at different moisture contents;
  - (b) Adaptation of fabric speed as per piece length and fabric structure;
  - (c) High heating and cooling rates in the gas stream;
  - (d) HT discharge via gas pressure reduction.
- Injection circuit, facilitating:
  - (e) Injection of dyes and chemicals into the gas stream;
  - (f) Different liquor loads for different types of goods varying in fibres and their construction;
  - (g) Liquor ratios, i.e. total amount of liquor/batch weight from 1 to 4.
- Calorific efficiency for heating and cooling derived in the forms of:
  - (a) Sum of individual values for textile, treatment liquor and machine parts while heating and
  - (b) Additional heat withdrawal by evaporation during cooling.

- The aerodynamic system and performance values of such machines hold out promise of higher productivity to the tune of about 100% on conventional jet dyeing machines, for a variety of goods.
- Water and energy requirements of airflow machines are only about 50% of conventional machines, thereby providing ecological advantages;

Table 8.5 gives a list of leading air jet dyeing machine manufacturers and their main machine models, a selection of which are discussed below.

#### *Airflow Synergy of Then, Germany*

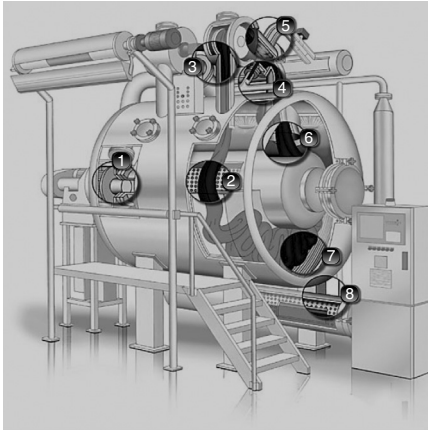
Figure 8.11 shows this latest aerodynamic HT piece dyeing machine for fabrics in rope form. Its parts are labelled 1–8 and have the following functions:

1. Aerodynamic transport: economical, frequency-controlled motor.
2. Safe fabric transport: optimum displacement and minimum crease formation are ensured by the aerodynamic drive.

*Table 8.5* Airjet dyeing machines

S. No	Manufacturers	Models
1	Alliance, France	Riviera Ventura
2	ATYC, Spain	Airtint EVO
3	Dilmenler (DMS), Turkey	DMS 03 HT Synchron Airjet
4	Flainox, Italy	HT Machine with Air Injection
5	Fong's, Hong Kong	Airsoft High Temperature
6	Hisaka, Japan	Air Circular
7	Laip, Italy	Airjet 2000 Air Water Flow 800
8	MCS, Italy	Airjet HT Airjet 2HT First Vento Universal Dyeing
9	Then, Germany	Airflow AFS Airflow AFE Airflow AFT Airflow AFA Airflow Lotus Airflow Synergy
10	Thies, Germany	Luft-roto Luft-roto plus Luft-roto plus SII Air stream

*Source:* Adapted from Nair (2001d); Nair and Pandian (2003c); Nair and Pandian (2005d); Nair and Pandian (2008c).



8.11 Parts of Airflow Synergy (Then). See discussion in text for explanation of parts.

3. Active fabric running control facilitates slip regulation, the exact monitoring of the fabric speed and protective fabric handling.
4. Unique rinsing method: short processing times with excellent rinsing through spraying with fresh water.
5. Maximum dyeing safety: aerodynamic fabric transport enables dyeing processes in a saturated steam atmosphere.
6. Optimised fabric storage: smooth plaiting guarantees excellent fabric displacement.
7. Dye liquor fabric separation: PTTE slide bottom ensures maximum gliding and protection of fabric surface.
8. Liquor sump: the 'Self Cleaner' filter system ensures free surface and reduces setting times between batches.

The main features of this machine are as follows:

- The patented aerodynamic system is based on the principle that the fabric transport is carried out by air only, which means that as opposed to a hydraulic dyeing machine, no dye liquor or aqueous medium is required to transport the fabric. The fabric is constantly in motion from loading to the batch end, even during the discharge and filling processes.
- Knits and woven fabrics from light up to heavy weight and virtually made from any fibre or fibre blend can be bleached and dyed without modifications or changes to the machine. The modular system allows tailor-made configurations which guarantee maximum efficiency.
- Machine offers previously unattainable economic and ecological advantages: unlimited flexibility with regard to all fibres (except pure wool) and fabric weights of 50–800 gm/m, lowest liquor ratios of 1:2 for

synthetic fibres and 1:3–4 for natural fibres, depending on the article and structure.

- Self-cleaning filter system, ensuring a lint-free surface which greatly reduces the setting times between batches.
- Energy savings of approximately 40% compared to hydraulic jet dyeing machines.
- Hot draining system, allowing draining at temperatures over 95°C while the fabric is in motion.
- A reduction in the overall process time of around 25%.
- Claims its ‘lowest water consumption and effluent represent an ecologically sound solution’.
- Operating temperature: max. 140°C at 3 bar overpressure.
- Operations are controlled by Then-Dynet unit consisting of a Window PC with touch screen and MCU (Main Control Unit).

#### *Luft-roto plus SII of Thies, Germany*

This air jet in the Luft-roto series, developed jointly with DyStar, has the following main features:

- Developed from the ‘internationally successful Luft-roto plus fabric dyeing machine’.
- Combines the ‘outstanding features of safe fabric transport and flexibility with new innovations in liquor transfer, liquor penetration and process technology’.
- The ascending fabric passes through the liquor nozzle before moving over the transport winch, in practice allowing liquor ratios as low as 1:3.
- Air transport system that ensures optimum plaiting of the impregnated material into the almost liquor-free, gravity-driven inner rotating chamber.
- Novel technology that reduces the process time and total energy consumption while at the same time enhancing the quality of the processed material.
- This ‘highly versatile’ machine can be used to process all types of fibres and their blends.

## **8.7 Atmospheric softflow/overflow dyeing machines**

These machines with their gentle softflow/overflow, without pressure or HT, are the most appropriate for delicate, sensitive and surface-designed fabrics. They have also been established as the most suitable dyeing machines for knitted fabrics, both circular and open width and terry towels. Due to increasing demand, a large number of manufacturers now produce this type of machine.

These machines have evolved from the traditional jet dyeing machines. The softflow/overflow fabric transport system in these machines is substantially different to the powerful ventura liquor jets transport system of conventional jet dyeing machines. In softflow/overflow machines, liquor overflows as free fall, aided only by gravity and with no pressure involved. The liquor carries the fabric along with it, with almost zero pressure on the fabric. These machines are ideal for dyeing sensitive and delicate fabrics and were indeed developed for this type of material. With their low liquor ratios and recovery systems, these machines are energy-efficient as well as cost-effective, and offer a reduction in the amount of effluent produced.

In order to make these machines versatile and universal, the overflow transport system is coupled with a jet transport system to produce jet/overflow machines that have a higher liquor circulation rate, a lower liquor ratio and a faster dyeing cycle. Many of the more recent machines are of this type and have the advantages of both jet dyeing and softflow/overflow dyeing systems. A variety of models are available to suit various loading capacities and space limitations. With the increasing demand for fashion fabrics that are sensitive and delicate and often have surface designs and effects, many innovations have been introduced to improve performance. Such improvements achieve gentle, damage-free fabric movements in the machine, better quality dyeing, better productivity, easier and more reliable operations and above all overall savings and operational economy in terms of water, power, labour, colour, chemicals and space, along with increased safety and less pollution.

These machines are specially designed to dye delicate fabrics that are prone to pilling and sensitive to superficial abrasion and over-tension; this type of fabric cannot be processed in the types of other rope dyeing machines described earlier. Compared with HT softflow/overflow machines, which will be described in the next section, these machines run at atmospheric pressure and hence can dye at a maximum temperature of only around 100°C. Dyes and conditions have to be selected accordingly. Table 8.6 gives a list of leading machine manufacturers and machine models, a selection of which are discussed below.

#### *FallFlow compact of Loris Bellini, Italy*

Figure 8.12 shows rope movement in the FallFlow Compact atmospheric softflow dyeing machine. The features of this machine are as follows:

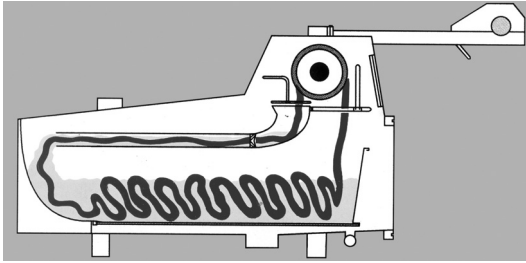
- The patented hydraulic 'FallFlow' system ensures a high level of liquor circulation, short dyeing times and uniform colour, while safeguarding the appearance and dimensional stability of the fabric.
- FallFlow is a softfall liquor distributor spanning the full width of the dyeing chamber. The liquor acts on the fabric only by gravity.

Table 8.6 Atmospheric softflow/overflow dyeing machines

S. No.	Manufacturers	Models
1	ACME, Taiwan	AM-SF Dual Flow
2	AKM, Taiwan	AK-REO Normal Temperature
3	Alkan Makina, Turkey	Overflow
4	Bellini, Italy	FallFlow Compact FallFlow FFL Fallflow Terry Ecomac
5	Brazzoli, Italy	Cameldyeing
6	Dalal, India	Turbosoft-AS
7	DMS, Turkey	DMS 02 ATM Softflow
8	Fong's, Hong Kong	Ecotech 38 Towel-38 Eco-38-Super
9	Harish (Pacific-Harish)	Softflow SF
10	Infab, India	Atmospheric Pressure Overflow
11	Krsna, India	K2002 Atmospheric Softflow
12	Laip, Italy	Mod.400 Overflow Mod.800 Water Flow 98°
13	MCS, Italy	Euro Flow Atmospheric Soft Flow SF 99 Low Temperature Soft Flow SF 99 Silk
14	Minox, Italy	Flow ATM Flow ATM Soft Duo Flow ATM
15	Noseda, Italy	Overflow Atmospheric
16	PMM, Turkey	Overflow Atmospheric Softflow Atmospheric Moonlight Atmospheric
17	Sclavos, Greece	Athena 2 Athena 2T Athena 2B
18	Texlink, China	SL Eco-Tech Softflow
19	Thies, Germany	Eco-flow 95 Soft 100 Soft-TRD/SoftTRD DSXL Mini-soft/Mini-softTRD
20	Tong Geng, Taiwan	Model NPL
21	Yamuna, India	Ecosoft

Source: Adapted from Nair (2001f); Nair (2001g); Nair and Pandian (2005f); Nair and Pandian (2008e).

- Fabric is gently lifted from the fabric storage chamber by a reel of large diameter, runs through the free-flowing high-flow rate liquor stream coming from the distributor and enters together with liquor, a U-section channel, which feeds fabric and liquor back to the storage chamber.



8.12 Rope movement in FallFlow Compact (Bellini).

- The lifting reel is designed to be at minimum distance from the storage chamber.
- In contrast with low flow rates at HP of many conventional machines, FallFlow has soft action and high liquor flow rate thereby making the machine ideal for dyeing all types of delicate fabrics like woollen, worsted wool, loop and loop-cut terry towels and acrylic and wool blends with cotton.
- Longitudinal layout of chamber favours a smooth and free-running motion of fabric from rear to front of machine and gentle liquor transport of material back to the reel.
- Fabric while occupying a large portion of the chamber gets opened up to the maximum to have no mechanical wear which could otherwise happen during the passage in the conventional narrow nozzle. For extremely sensitive fabrics, a machine with a lifting reel with a flat and smooth surface can be used. The inside of the storage chamber and transport channel can be Teflon-coated, on request.
- The hydraulic circuit of FallFlow Compact is designed and engineered for very high liquor flow rate of two to five times that of other machines at low head pressure. The circulation pump is of axial (turbine) design equipped with maintenance-free mechanical seals. The axial pump is self-cleaning and hence does not require filters that affect flow rates, with the resultant benefits of high machine efficiency and savings in labour. There is a liquor flow rate regulation valve.
- Electric power consumption is optimised by using an AC power frequency converter with an accuracy of 1 rpm. The absorbed power varies with the torque of the motor with average power savings of 30%.
- Simple, user-friendly operations that can be learnt in only a few hours.
- A variety of fabrics weighing from 150 to 1200 gm/m can be dyed with no need for special adjustments to the machine.
- For dyeing ultra-light fabrics, a twin-chamber version with rope separation system ensuring smooth fabric feeding is available. This machine



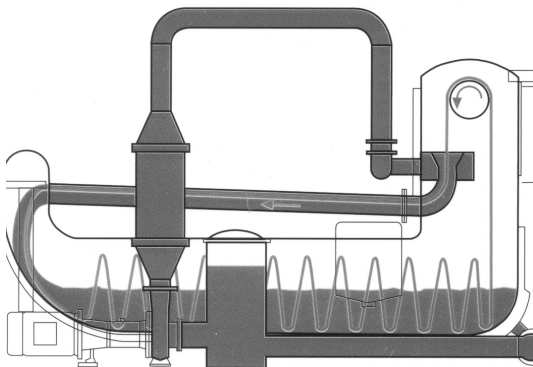
has full internal access through its large front door for inspection, cleaning and maintenance.

- The machine has an indirect multi-tubular heat exchanger, located at the bottom of the storage chamber and separated from the plaited fabric. This high surface heat exchanger, covering the entire chamber, ensures perfectly uniform liquor temperature distribution. This exchanger is also designed for high cooling and heating rates. Heating from 15 to 80°C is at 3°C/min, 80 to 98°C at 2°C/min and cooling from 98 to 80°C is at 2°C/min.
- Inspection window and internal lighting.
- FallFlow Compact machines are designed with a Computer Aided Designing (CAD) system and are of modular construction.

#### *Overflow 400 of Laip, Italy*

Figure 8.13 shows the rope movement in this machine, which has the following features:

- Suitable for dyeing all varieties of fabrics with weight between 80 and 800 gm/m<sup>2</sup>.
- Specially designed front hatch facilitates machine cleaning.
- Bath ratios are from 1:5 to 10; temperatures up to 98°C.
- Efficient use of available energy and optimised water circulation guarantee environmental quality.
- Perfect duplication of cycles through automated processes.
- Machines can be installed to work singly or in tandem hook-ups.



8.13 Rope movement in Overflow 400 (Laip).

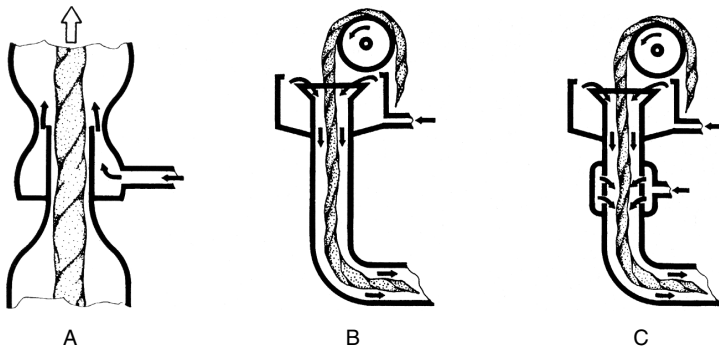
## 8.8 HT softflow/overflow dyeing machines

These batch rope dyeing machines are popular HT dyeing machines, particularly for dyeing polyester and its blends. Figure 8.14 shows the three fabric transport systems used in jet dyeing machines, labelled A, B and C (Anon, 1989). A shows the system in the original versions of jet dyeing machines, such as ATYC's vertical dyeing machine 'Texajet', wherein the fabric is transported solely by means of liquor jets hydraulically based on the ventura principle, the original patent of which belongs to Burlington Industries, USA.

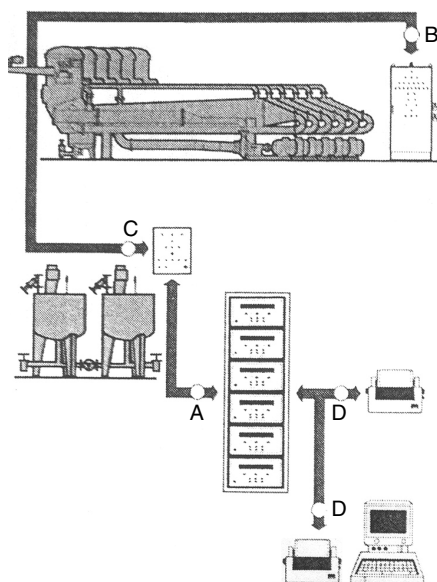
B shows the overflow system, first introduced by the Japanese, in which the liquor flows as free fall without pressure. This system is ideal for dyeing sensitive fabrics that cannot be dyed without damaging them in traditional jet dyeing machines. ATYC's 'Fluxsuau' overflow machine was first exhibited at ATME 1973 in Greenville, USA.

Changes to the overflow system were also required due to its slow gravity aided circulation and its need for a high volume of liquor. In order to overcome these drawbacks and to make the machine flexible and cost-effective, the jet/overflow system, C, was developed.

Figure 8.15 shows the concept of modern automatic dyeing using machines of the fifth generation onwards with the various sections labelled. Modern dyeing machines have gentle action and are safe for both the goods and the operator. They have a very high degree of automation, with only loading and unloading performed by the operator. With microprocessor control, these machines are 'dyeing robots' with the dyeing technician only entering the recipes and the selected dyeing method into the process control system.



8.14 Fabric transport systems. A: Jet system; B: Overflow system; C: Jet/overflow system.



8.15 Automatic dyeing. A: Microprocessor; B: Dyeing machines; C: Automatic dye-kitchen and D: Computer, printer, data processing system.

Table 8.7 provides a list of leading machine manufacturers and their main machine models, a selection of which are presented below.

#### *Multi-Nozzle Softflow (B) of Devrekha, India*

This machine has the following features.

- Flexibility: ability to work at high and low temperatures and also as a softflow or jet dyeing machine. This makes the machine versatile and able to process all types of fabrics.
- Four nozzles: Nozzles 3 and 4 are of big diameter and fixed with individual flow control valves. The first main nozzle is adjustable, and by increasing and decreasing the gap of nozzle, flow and pressure will increase and decrease according to the requirements of the fabric. To run this machine as a softflow machine, the gap should be increased in order to decrease the pressure and increase the water flow. Under these conditions, all three nozzles will work as a softflow and water flow control system with individual control valves to facilitate processing of all types of fabrics.
- Other features are ultra low liquor ratio of 1:1 (wet fabric); can dye both woven and knitted fabrics of 30–450 gm/m<sup>2</sup>; temperatures up to 140°C; capacities from 50 to 2000 kg.

Table 8.7 HT softflow/overflow dyeing machines

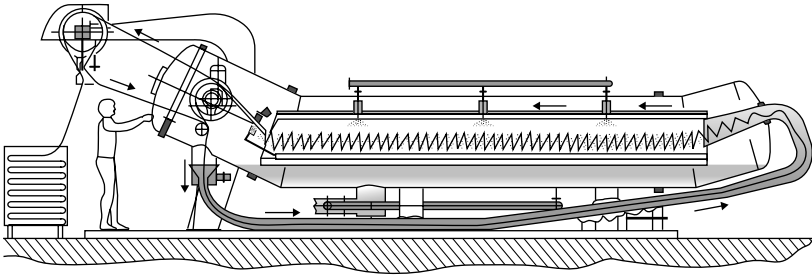
S. No.	Manufacturers	Models
1	ACME, Taiwan	AM-SF Dual Flow
2	AKM, Taiwan	AK-SL Dual Flow AK-ISL Dual Flow Rapid
3	Alkan Makina, Turkey	03C HT
4	Anjani, India	Long Tube Soft Flow 'O' Type Soft Flow
5	ATYC, Spain	Rapidsuau F/FL Rapid Stretch
6	Brazzoli, Italy	Saturno HTF
7	Devrekha, India	Multi-Nozzle Softflow (A) Multi-Nozzle Softflow (B)
8	Dilmenler (DMS), Turkey	DMS 02 HT Softflow
9	Flainox, Italy	PIROGA GHBLI/Flow HT
10	Fong's, Hong Kong	Eco-8 Multi Rope Soft Towel-8 High Temperature
11	Hisaka, Japan	CUT-MF Type (Mild Jet Flow)
12	Infab (Texfab), India	HT/HP Eco-Softflow Single Tube/Multi Tube
13	Krsna, India	HT Soft Flow Long Tube Model K2002 RHL HT Soft Flow Model K2002 RH
14	Laip, Italy	600/HP Soft-flow 800 HT Water Flow 900 HT Overflow
15	MCS, Italy	Long Horn Flow Jet HT Softflow SF 100 Horizontal
16	Memnun, Turkey	Conti Dye HT
17	Minox, Italy	Flow PRT Soft
18	PMM, Turkey	Softflow HT
19	Then, Germany	Thenflow
20	Thies, German	Soft-TRD Soft-TRDDS
21	Yamuna, India	HT/HP Softflow

Source: Adapted from Nair (2001e); Nair and Pandian (2005e); Nair and Pandian (2008d).

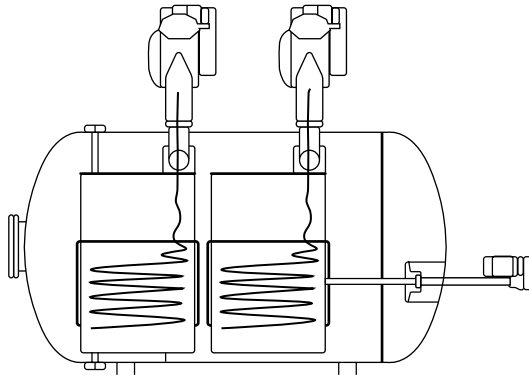
### *PIROGA of Flainox, Italy*

Figure 8.16 shows this new HT machine for rope dyeing with fabric out of bath. The special features of this machine are as follows:

- Revolutionary concept and design with fabric always being dyed above the bath with sprays from the top, in a bath with a liquor ratio of 1:4.
- Low liquor ratio results in less dyeing time and savings in costs.



8.16 Parts and rope in PIROGA (Flainox).



8.17 Innodye basket system (Brazzoli).

- Positive mechanical conveyance system inside the autoclave, operated independently of the dyeing bath, advances the fabric. It consists of a bar-work element (Patented) operating with a rotary action that lifts and then deposits the material so that it advances with each action.
- Squeezing effect on fabric allowing for a natural bath/fibre exchange effect (sponge effect) aided by special sprinklers positioned all along the route.
- Special transportation system with integrated cooling-rinsing system that leads to highly efficient washing cycles thereby giving drastic reduction in water and time factors, claimed to be only a tenth of that of standard machines.
- Coupling possibility for up to four machines.

## 8.9 Machines to dye fabric in rope/open-width form

*Innodye of Brazzoli, Italy*

Figure 8.17 shows this innovative jet dyeing machine basket system of rope opening with the following salient features:

- Innovative transitional bath motor using a mobile basket with an alternated transversal motion.
- Device positioned inside machine with automatic self-adjustable system to control its speed synchronised with fabric driving wheel.
- Rapid and homogeneous mixing of dyes and chemicals and their rapid diffusion into the fabric, resulting in reduction in dyeing time, reduction in foaming and perfect dyeing.
- Innovative ‘double injection’ dosing system, resulting in faster dosing that even prevents hydrolysis of reactive dyes. This offers ecological and economical advantages.
- Ability to dye very delicate and sensitive fabrics – multi-sectional area developed longitudinally allows reduction in bath ratio and a more homogeneous contact between fabric surface and bath.
- Integrated software system for programming and control of operations.

## 8.10 Semi-continuous and continuous open-width dyeing machines

Semi-continuous and continuous open-width fabric dyeing machines are necessary to produce bigger lengths of uniform, high quality shades economically. A comparison of the features of continuous dyeing with those of batch dyeing is given in Table 8.8 (Nair, 1999b; Nair, 2002; Nair and Pandian, 2008f). In these machines, which are produced by a large number of manufacturers, the dye application padding mangle is the most important component for shade uniformity, avoiding selvedge to selvedge or centre to

*Table 8.8* Continuous dyeing vs batch dyeing

Features	Continuous dyeing	Batch dyeing
Shade uniformity	High degree over width and length and reproducibility	Possibility of batch to batch shade variation
Quality of dyeing Suitability for garments and uniforms	Better Suitable	Good Not suitable
Crease defects Production	Can be controlled High due to short through times	Difficult to control Less due to long dyeing times as it is broken-up in between
Labour requirement	Less	More
Process cost	Less	More

*Source:* Adapted from Nair (1999b); Nair and Pandian (2008f).

selvedge shade variation. In these machines any of the following dyeing processes may be used:

- Cold Pad-Batch
- Pad-Dry-Pad-Steam
- Pad-Steam (all in all)
- Pad-Dry-Thermofix
- Pad-Steam (Wet/Wet)
- Pad-Steam-Pad-Develop
- Pad-Steam-Pad-Thermosol.

The units of equipment are as follows:

- Padding mangles for application of dyes and chemicals
- Air passage unit for dye/chemical penetration
- Infrared unit for pre-drying
- Hotflue or float drier for drying/thermofixing/thermosoling
- Booster for application of chemicals
- Batching and batch rotation unit for colour fixation at room temperature
- Reactor steamer for steaming/air passage
- Units for rinsing/oxidation/soaping.

The semi-continuous dyeing process is very popular, useful and economically viable. It employs reactive dyes in the 'Cold Pad-Batch' process for dyeing cellulosics. The steps involved in this technology are pad with dye and alkali–batch–dwell–rinse–soap. The units of equipment used are padding mangle (padder), batching unit with batch rotation and soaper for rinsing, soaping and drying. The equipment used for the first stages, namely, padding and batching, is popularly known as a cold pad-batch (CPB) dyeing machine.

The continuous dyeing process involves more steps and uses units such as padders, boosters, Infra Red (IR) pre-driers, driers, steamers, air passages and washers (Shore, 1979; Ellis, 1984; Hyde 1998). The colours that can be used include reactive, vat, sulphur, azoic, pigment and disperse dyes. Table 8.9 (Nair and Pandian, 2008f) provides a list of the leading machine manufacturers and their machine models, a selection of which are discussed below.

#### *Ben-Colour of Benninger, Switzerland*

Figure 8.18 shows Ben-Colour, the continuous pad-dry and pad-steam dyeing range that has modules or sections for colour padding, penetration and IR-pre-drying, drying and/or thermofixation, cooling, chemical/colour

*Table 8.9* Semi-continuous and continuous dyeing machines

S. No.	Manufacturers	Models (Semi-continuous (SC) and Continuous (C) dyeing Machines)
1	Benninger*, Switzerland	Ben-Colour (SC and C)
2	Brückner, Germany	Pad-Dry/Thermosol line (C)
3	Brugman, Netherlands	Pad-Steam range (C)
4	Reisky-Dhall, Brazil-India	Continuous Pad Dry/Pad Batch dyeing range (SC and C)
5	Dhall, India	Cold pad-batch machine (SC) Continuous Over dyeing range for denim (C)
6	Erbatech, Germany	Scout-color Padder (SC) Supraflor Carpet dyeing machine (C)
7	Fleissner, Germany	Continuous Carpet dyeing range (C)
8	Goller, Germany	Goller-Colora (C)
9	HTP Unitex (Mezzera), Italy	Pad Steam dyeing line (C)
10	Küsters*, Germany	DyePad (SC and C)
11	Memnun, Turkey	Dyeing machine for indigo blue (C)
12	Monforts, Germany	Thermex 5500 (SC and C) Econtrol continuous dyeing (C)
13	Morrison, USA	Cold pad-batch range (SC) Pad Steam range (C) Thermosol Pad Steam range (C)
14	Swastik, India	CP Dyeing (SC) Continuous dyeing plant (C)
15	Yamuna, India	Continuous dyeing plant (C)

\*Benninger has taken over Küsters Textile and Subsidiaries of Küsters Far East and Küsters Shanghai in 2007 but no changes for Küsters-Zima, USA and Küsters Calico, India

Source: Adapted from Nair and Pandian (2003c); Nair and Pandian (2003d); Nair and Pandian (2005g); Nair and Pandian (2008f).

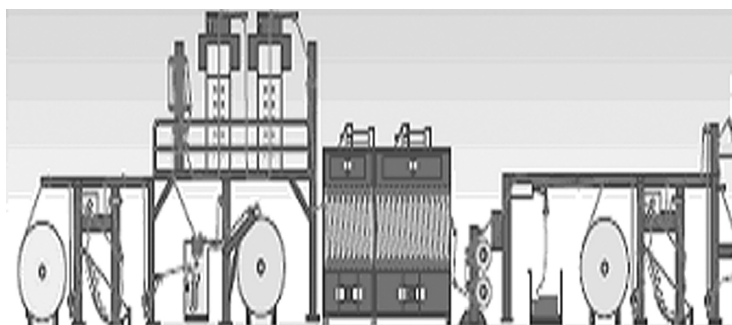
padding (one- or two-bath), steaming, rinsing and oxidation/soaping and finally drying.

The possible applications are as follows:

- pad-dry/pad-steam-wash process with reactive or vat dyes on cotton
- pad-thermosol-pad-steam-wash process with reactive or disperse dyes for cotton/polyester blends
- pad-thermosol-pad steam-wash process with vat and disperse dyes for cotton/polyester blends
- pad-dry-thermofix-wash process with reactive dyes on cotton
- pad-dry-pad-develop-wash process with azoic dyes on cotton
- cold pad-batch-wash dyeing process with reactive dyes on cotton.

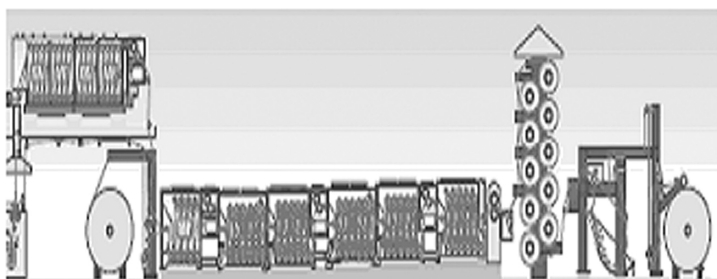


PENETRATION AND  
IR-PREDRYING



PADDING- -DRYING AND COOLING - PADDING - →  
THERMOFIXATION

STEAMING -

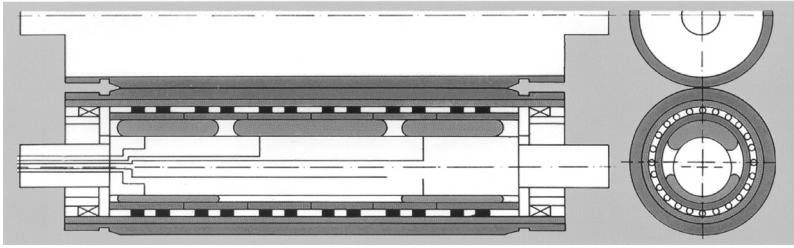


→ RINSING AND OXIDATION/SOAPING - DRYING

8.18 Sections of Ben-Colour continuous dyeing machine (Benninger).

The fabric feed system incorporates a fabric accumulator for automatic roll change to prevent colour differences resulting from machine stoppages. The dyeing padder has a flexible Bicoflex roll to guarantee a uniform pick-up, independent from production speed and fabric weight. Linearity of the nip line is ensured despite the freely adjustable nip pressure. Figure 8.19 shows the construction details of Bicoflex roll. Its features include the following:

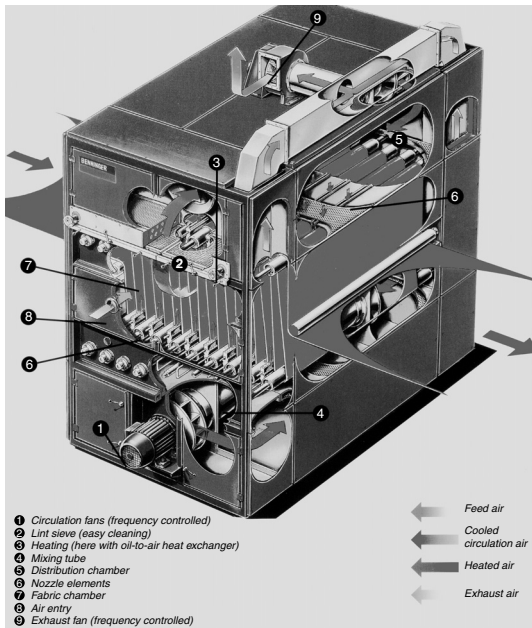
- Uniform linear liquor application from beginning to end of dyeing operation;
- Uniform squeezing pressure within the range of fabric including thick and narrow webs (without selvedge pressure);
- No side-to-centre shading due to smooth treatment of selvedges;
- Reproducibility of all dyes and chemical applications;
- No cambering of the squeeze rolls;
- Simple operation and control due to clear design;



8.19 Construction details of Bicoflex roll (Benninger).

- Low energy consumption and short return of investment;
- Reduction of setting-up times through the effective roll washing system;
- Completely reliable and maintenance-free operation;
- Special displacement elements and lay-on rollers in the U-shaped troughs or in economic troughs permit low liquor content, resulting in fast liquor exchange and preventing any undesired changes in concentration. All troughs can be raised, lowered and tilted pneumatically. Further, the well-known wedge-shaped trough can be installed for special applications. Fabric is guided in this case from top to bottom through a horizontal roller nip. Alternatively, passing through the trough is possible.
- Padded fabric is pre-dried in Thermray infrared pre-dryer having the following features:
  - High drying capacity without migration;
  - Robust metal fibre IRG-gas radiators with 2, 4 or 6 burner rows with individual burner switches to control performance;
  - Special burners with rapid warming and cooling capability;
  - Durable metal fibre burner can reach a temperature of 1050°C;
  - Burner regulated from 50 to 100% by controlled gas flow and frequency-controlled burner air (optional);
  - Flap control to regulate exhaust air;
  - Multi-circuit safety system for stopping the machine. No moving parts needed. Immediate cooling of the special burners by admitting and exhausting cooling air.

The pre-dried fabric moves next to the drying and/or thermofixation unit, Thermfix, shown in Fig. 8.20. This Hotflue Thermosol is built with 'optimised drying conditions with leading technology'. In this unit, crease-free fabric transport and low tension are ensured by frequency-controlled individual AC-drives. Load cell technology is used for measuring the fabric tension. Individual single AC-drives guarantee reproducible low tension conditions which are maintenance-free and reliable. There are no clutches,



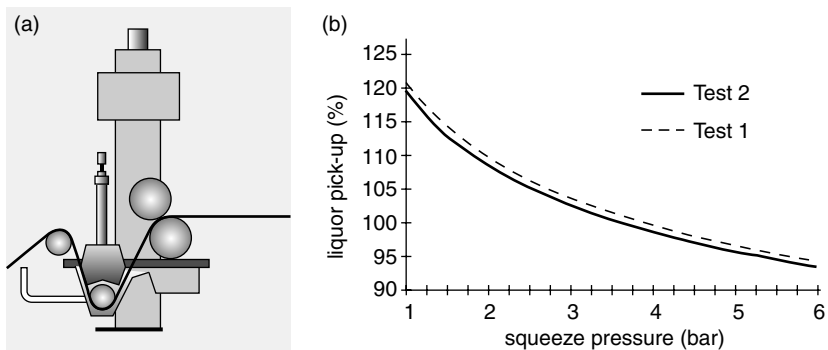
8.20 Thermfix HotflueThermosol (Benninger).

chains or belts. Cleaning and maintenance are also minimised, as the lint sieves can be easily cleaned even during operation. All guide- and drive-rollers are equipped with enclosed lifetime lubricated bearings which are mounted outside the insulated dryer chamber. The grease used is resistant to HT and is suitable for thermosol processes. Grease drops on the fabric are a thing of the past. In areas where dye-deposition can occur, the rollers are Teflon-coated. High uniformity of air flow, air temperature and air humidity over the length and width of the fabric in the Thermfix chamber are ensured by two diagonally located frequency-controlled circulation fans (1). Air flows from the fabric chamber through the lint sieve (2) and is heated (3) either by oil-to-air or steam-to-air heat exchangers or direct gas heating. From the mixing tube (4) air enters the big distribution chamber (5). Air is distributed over the length and width and uniformly pressed through nozzle elements (6) into the fabric chamber (7). These nozzle elements have vertical air exit for uniform air and temperature distribution without heating of rollers. In each chamber, air quantity and temperature are controlled. The conditions are set appropriate for fabric weight, fabric construction, fabric composition (cotton, cotton/polyester, polyester, etc.), pick-up, etc., to prevent migration. Each chamber is suitable for drying (pad-dry) or for thermosetting (pad-thermosol) processes. It is important that the exhaust air should be removed in a controlled fashion in order

to optimise the drying conditions. Frequency-controlled radial fans (8) are used to adjust the amount of exhaust air, while an automatic closed loop control with an electronic moisture probe in the exhaust air stream is available as an option. The feeding air enters the fabric chamber through the side slide gates (9). The entire chamber body is fully insulated, and the side walls are all built in the form of doors which are equipped with special slots to prevent heat transfer. This excellent insulation guarantees the lowest possible heat loss and is one of the reasons for the low overall energy consumption of the range.

After drying and/or thermofixation, the fabric moves on to the cooling zone, and then on to the Ben-booster unit (Fig. 8.21a) positioned outside the steamer for chemical padding to ensure uniform liquor application. The dipping length is kept short and no heating is required but good penetration into the fabric is achieved. Replacing the steamer inlet water lock with the booster would result in heating of the fixation liquor, which would decompose the hydrosulphite used in chemical pads for vat dyes. The booster's squeezer consists of two ground soft rubber rollers, where it is possible to cover a large pressure range with a parallel nip. The data presented in Fig. 8.21b show that a wide range of liquor pick-up is achievable with this booster squeezer: indeed, any specific liquor pick-up can be set for all fabrics. In the one-bath pad-steam process such as that used for sulphur dyes on cotton, this padding Ben-booster will have colour along with chemicals.

The colour and chemical padded fabric is then subjected to saturated steam fixation in a Reacta steamer. This unit has modular sections, each able to contain 25 m of fabric and with either a horizontal or a vertical feed. To prevent water dripping, the inlet lips of the dyeing steamer are indirectly heated and the escaping steam clouds are extracted to prevent formation of condensate. Air-free operation is ensured by monitoring the temperature



8.21 (a) Ben-booster and (b) its squeeze vs pick-up (Benninger).

outside and below the bottom level of the steamer. Any deviation in temperature immediately leads to an increase in the steam supply. The exact saturation of the steam is achieved in the steam conditioning unit. Pressure is reduced independently of the flow rate and the throttled steam is then cooled and saturated in a water cooler. A control valve adjusts the steam supply corresponding to the temperature. A water lock at the steamer exit is indispensable for airtight closure, and the passage of hot cloth through this water lock heats the water. Chemicals also accumulate here. In the case of vat dyes, HT and higher levels of hydrosulphite and caustic soda lead to stripping of colour or at least to tailing. For this reason, the water lock on Benninger's steamer has a temperature-controlled fresh water supply to ensure ample dilution and constant conditions.

The next element of the dyeing line is the washing section for rinsing and oxidation/soaping. This stage is essential for proper completion of the dyeing process and for obtaining good dyeing results. The various groups of dyes require different after-treatment processes (Table 8.10), which the washing section should be able to accommodate.

Benninger uses the tried and tested Ben-Extracta washing compartments, which are able to fulfil the requirements of all process stages. Rinsing processes are carried out in single loop washing compartments and dwell processes in double loop compartments. The treatment steps differ for different classes of dyes, with some requiring more steps. For this reason, some washing compartments may be divided into independent sub-compartments. These divided Beco-flex washing compartments allow two separate treatment steps in one compartment. The Extracta press rolls ensure good bath separation.

The last section of the dyeing range is dedicated to drying the dyed and rinsed fabric on a cylinder drying range.

*Table 8.10* Dyeing after-treatments

Substrate	Dyes group	After-treatments
Cotton or viscose	Reactive	Rinsing – soaping – rinsing or hot counter-flow washing
	Vat Sulphur	Rinsing – oxidising – soaping – rinsing rinsing – neutralizing – oxidising – soaping – rinsing
Cotton/polyester blends	Reactive/disperse	Rinsing – soaping – rinsing
	Vat/disperse	Rinsing – oxidising – soaping – rinsing
Polyester	Disperse	Rinsing – reduction-clearing – soaping – rinsing

*Source:* Adapted from Nair and Pandian (2008f).

Benninger's dyeing ranges are equipped with a good level of automation. Water and chemical feeds are automatically controlled based on cloth weight and production parameters via inductive flow meters and control valves. Important machine settings are monitored and controlled by a Siemens PLC control system used for both drive and process control. The latest technology AC-drive system guarantees low tension and crease-free cloth transport. Further automation is an option in the shape of an independent recipe management programme or connection to a host computer system.

*Continuous pad dry/pad batch dyeing range of Reisky-Dhall, Brazil-India*

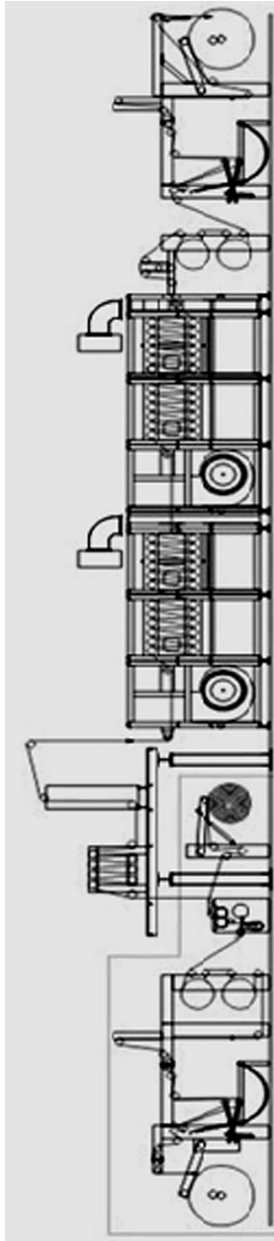
Figure 8.22 shows the parts and fabric movement of this range. Its main features are as follows:

- Suitable for dyeing cotton, synthetics and blended fabrics in open width.
- Equipped with Reisky-Dhall Dyeing Padder with two hydraulic controlled deflection rolls to guarantee even and uniform dyeing across entire width.
- Can be used as cold pad batch dyeing and pad-dry range; versions available for fabric widths up to 3200 mm.
- Scrays are provided at inlet and outlet for continuous operation.
- Large diameter, i.e. 200 mm, guide rolls are provided for creaseless operation; E+L cloth guiders.
- Colour dosing pumps developed by Prominent, Germany.
- Gas fired Infrared Pre-Drier is provided to avoid colour migration.
- Moisture Controller developed by Pleva, Germany is incorporated for precise and uniform control of moisture addition by steam inside Hot Flue Drier.
- Total package, i.e. PLC, Touch Screen, Invertors, Motors, etc., are from Adolf B Bockemueht GmbH & co, Germany (ABB) or equivalent, for total process control and easy operation.

*Scout-color Padder of Erbatech, Germany*

This padder is for semi-continuous dyeing and has the following features:

- Advanced tension control system allows all cellulosic fabrics and blends to be dyed with reactive dyes in open-width form. Formation of creases or pills is avoided. Fabrics of high elasthane contents can also be dyed without any problems.



PADDING - BATCHING - DRYING/FIXING/THERMOSOLING - PLAITING/BATCHING

8.22 Parts and cloth movement in continuous pad dry/pad batch dyeing range (Reisky-Dhall).

- Equipped with a modern automated self-cleaning system that allows a fast and economic processing even for smaller production lots.
- Pad-batch dyeing method brings additional advantages in terms of water and energy consumption.

*DyePad of Küsters, Germany*

This DyePad is very useful for both semi-continuous and continuous open-width dyeing. It has the following features:

- Claimed to be ‘the Brand-new Machinery Generation’, it provides ‘optimised dyeing with an increased operation range’ incorporating innovations ‘at the Swimming Roll Küsters, the rubber covering (BlueNip), the modular fabric guiding system, the drive system and the modern integrated control system’.
- Two horizontal, parallel Swimming Rolls with a doubled correction potential (Fig. 8.23). The S-Rolls are covered with the new BlueNip rubber covering, which is equipped with a universally applicable surface suitable for all dyeing processes. The BlueNip rubber covering also has high chemical resistance.
- Equipped with a reverse fabric guide suitable for both woven and knitted fabrics and optimised troughs with integrated heat exchanger.
- ‘Maintenance-free drive system and the new decentralised control system as well as the high profitability turns the Küsters DyePad into a padder which is tailor-made for all market requirements’, besides taking all relevant ecological aspects into consideration.



8.23 S-Rolls (Küsters).



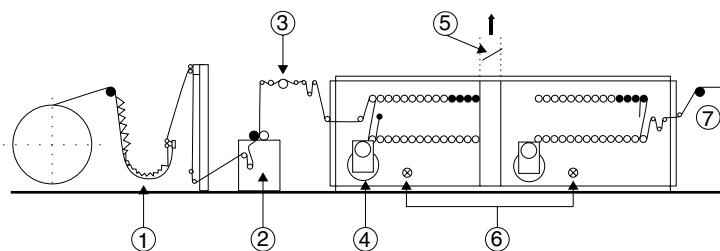
*Econtrol continuous dyeing of Monforts, Germany*

Figure 8.24 shows the Econtrol continuous dyeing range. Its features are as follows:

- Simple, rapid, innovative and economical continuous dyeing process for cellulose fibres with reactive dyes using minimum chemicals, developed by Monforts and BASF (Now DyStar). Process does not require process chemicals such as urea, sodium silicate, sodium hydroxide and salt: sodium bicarbonate is sufficient, thanks to the development of the Thermex Hotflue dryer with moisture content control and injection.
- Machine configuration (Fig. 8.24) consists of: fabric inlet; padding mangle for dye application; wetting unit to provide adequate moisture in Hotflue chamber; Thermex Hotflue for dye fixation; unit for measuring and controlling chamber climate; steam injection unit; outlet section and washing unit. IR-drier can be incorporated for beneficial use while dyeing heavy fabrics.
- Additional advantages include the absence of batching/rotating stations, extended machinery life due to avoidance of harsh chemicals such as salt and silicate and energy efficiency by optimum humidity control.
- In short, 'a simple, economic, efficient, environmentally friendly, energy saving and controlled process of continuous dyeing'.

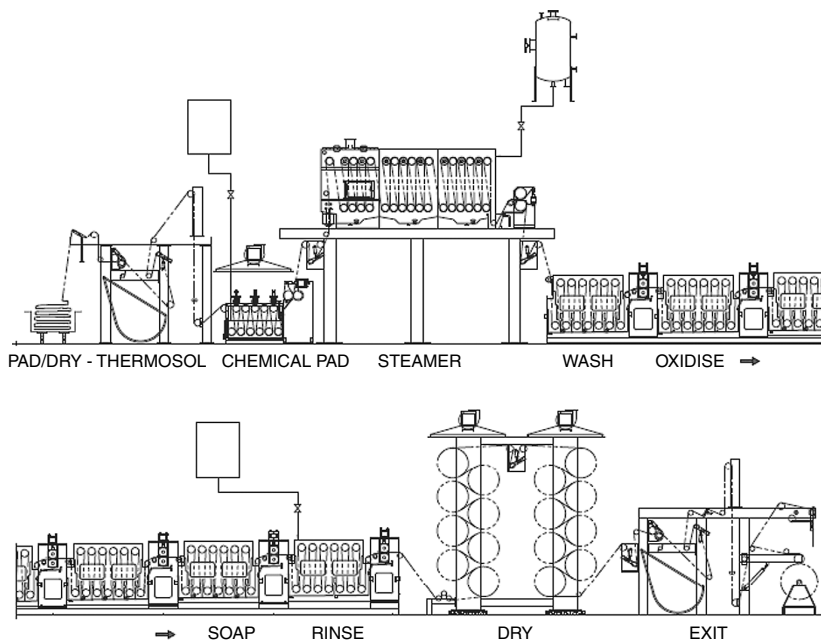
*Universal continuous dyeing range of Yamuna, India*

An abridged diagram of this machine is shown in Fig. 8.25. This machine has been designed by the author for continuous dyeing using all classes of commonly used dyes such as vats, reactives, sulphurs, azoics, pigments, mineral



- |                       |  |
|-----------------------|--|
| 1. Feeding section    | 5. Measuring - and control unit (chamber atmosphere) |
| 2. Pad mangle         | 6. Steam injection unit                              |
| 3. Wetting unit       | 7. Wash-off range                                    |
| 4. THERMEX R hot-flue |  |

8.24 Econtrol continuous dyeing range with process details (Monforts).



8.25 Universal continuous dyeing range (Yamuna).

khaki (MK) and disperse dyes (Nair, 2007). The features of this range are as follows:

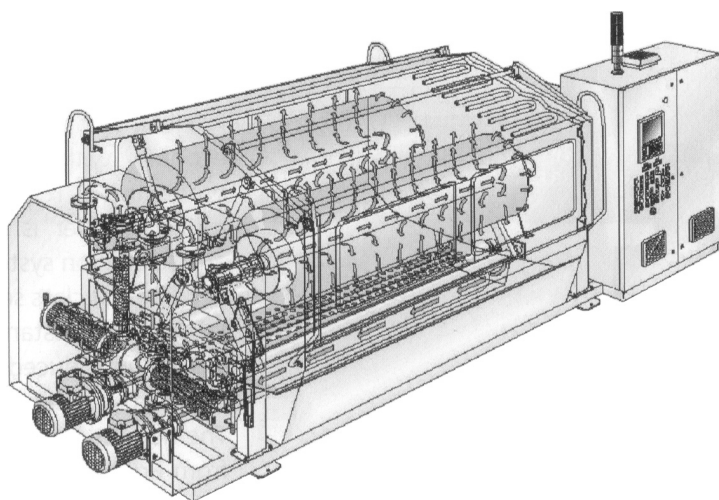
1. Single/double colour padding with a scray in between for giving dwell of the padded fabric. This step is helpful, especially for MK dyeing of thick fabrics, for full and proper penetration of colour and for colour economy.
2. Pre-drying with IR heaters, as an option, for preventing migration and for boosting dryer productivity. A three-pass, four-section float dryer is ideal for final drying or for drying and thermosoling for disperse dyes.
3. Chemical treatment (development) compartments, generally two, for hot caustic soda treatment in MK dyeing.
4. Chemical pad with two-bowl mangle and jacketed shallow trough having continuous pad liquor feeding arrangement.
5. Steamer with steam lock at entry and water lock at delivery, with control of temperature, speed and fabric tension.
6. A five-compartment range for washing, oxidising, soaping and rinsing; closed ones for soaping and rinsing with proper fabric squeezing (mangling) between compartments and after the fifth compartment.
7. Double stalk cylinder drying range with expander assembly at entry and batching/plaiting arrangement at exit.

## 8.11 Future trends

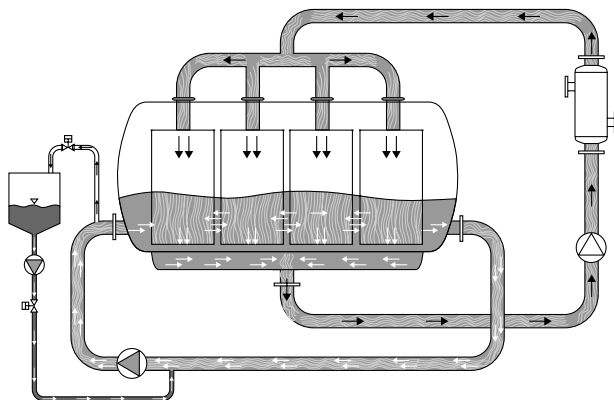
To meet the ever-growing concerns surrounding environmental conservation and energy consumption, future machines will have even lower M:L ratios (lower water requirements for processing and a reduction in the amount of effluent generated) with water recovery and energy (heat) reuse systems. It could also be expected that machines such as the 'Beam Jigger', a combination of autoclave and jigger, will substantially reduce the dyeing time by as much as 50%, with a similar reduction in water and energy consumption. Electronic equipment used in dyeing machines will be upgraded to optimise its controlling function and automation.

Brazzoli of Italy is developing a beam jigger, a patented prototype of which was exhibited at ITMA 2007 in Munich (Fig. 8.26) (Lempa, 2007). This batch open-width dyeing machine is a combination of autoclave and jigger. Designed with a novel liquor flow system, it reduces dyeing time by about 40–50% with a resultant reduction in water and energy requirements, and is the forerunner of future machines that will provide optimum interaction between fabric and liquor, leading to even faster dyeing processes. Brazzoli's latest Innoflow exl machine has a transversal system (Fig. 8.27) inside its autoclave leading to an innovative transversal flow of liquor which guarantees optimum consumptions of water, steam and energy while giving better quality dyeing in less time.

The German company Then has brought out a new Airflow Synergy/G2 (Fig. 8.28) dyeing machine with changes in the design of the fabric storage chamber, allowing strands of higher loads to be run, thus causing a further



8.26 Internal view of beam jigger (Brazzoli).



8.27 Translational flow in Innoflow exl (Brazzoli).

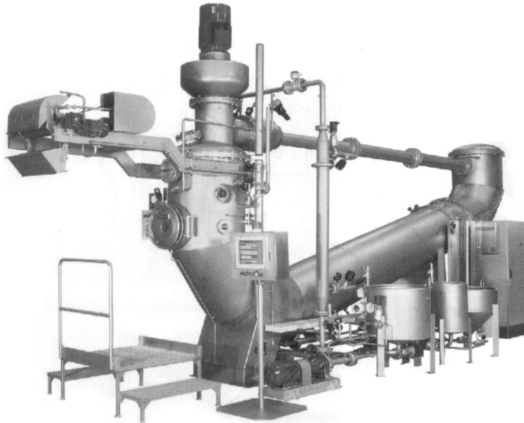


8.28 Airflow Synergy/G2 (Then).

sizeable reduction in water and energy consumption, to the tune of 20%, with benefits in terms of cost and ecological considerations. Similar features are also present in Fong's new ECO-6-Super rope dyeing machine (described earlier under batch rope dyeing, Fig. 8.7). Then is also in the process of developing the Airflow machine, which will be used to dye highly elastic as well as very sensitive or delicate textiles, such as those with up to 50% elasthane and knitted products. Its Airflow Lotus (Fig 8.29) is the first of these machines, and is currently being tested.

Monforts of Germany has brought out a new Thermex (Fig. 8.30) hot-flue dye development machine with variable height adjustment for the upper and lower rollers of its chamber, providing improved economy and increased productivity.

Further developments in machinery in collaboration with dyestuff manufacturers will also take place. These are likely to be along the same lines as Econrol (described earlier under continuous dyeing; Figs. 8.24 and 8.29),



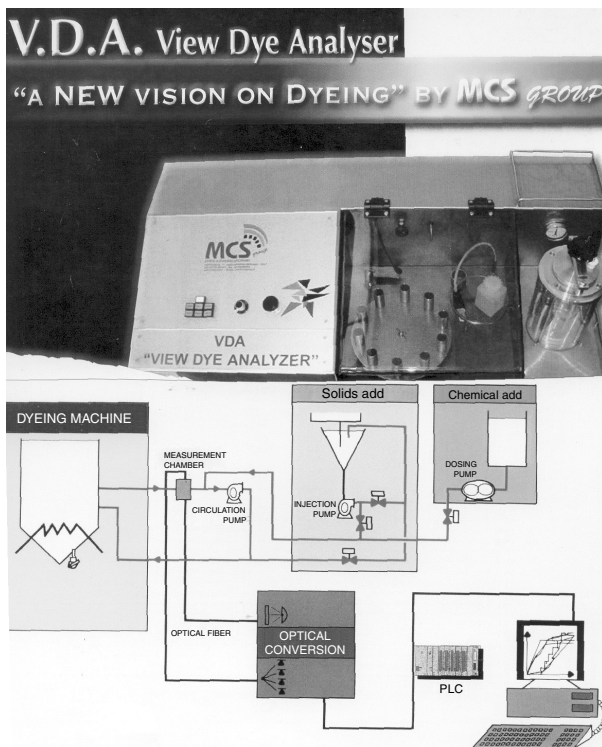
8.29 Airflow Lotus (Then).



8.30 Thermex 6500 (Monforts).

considered to be the most modern continuous dyeing concept jointly developed by Monforts and DyStar of Germany to achieve savings in chemicals, energy and process time with added environmental benefits. Fong's have also joined with DyStar to successfully develop its ECO-6-Super HT dyeing machine (described earlier under batch rope dyeing, Fig. 8.7) for controlled coloration with Remazol RGB dyes. By adopting the well-proven liquid separating and fast circulating technology, this machine achieves an extra low liquor ratio for reactive dyeing. The benefits claimed include a 21% savings in production costs (steam, water and electricity) compared with conventional HT dyeing machines, as well as superior quality dyeing with excellent reproducibility.

MCS Group of Italy has recently introduced its View Dye Analyser (VDA) (Fig. 8.31), a laboratory machine that allows the simulation of the



8.31 View Dye Analyser (MCS).

programme of a production dyeing machine and shows graphical curves representing the behaviour of the colour (on four optical filters), temperature and pH. Its components and functions are shown in the same figure. This laboratory machine thus optimises dyeing cycles by offering savings in time and improvements in quality; reduces the need for corrections (facilitates correct dyeing first time); optimizes consumptions of dyes and auxiliaries; and reduces energy consumption and polluting liquids. It therefore offers both economic and ecological benefits.

Cleaner and greener dyeing technologies such as the use of electricity in vat dyeing, ultrasound energy and Radio Frequency (RF) radiation will make progress by overcoming the present prohibitive cost involved in production scale dyeing machines. The electrically induced dyeing processes and machinery for vat dyeing developed by Krantz and SMH (Fig. 8.32) claimed advantages both in economy and ecology.

Machines dyeing fabric under positive conveyance from above the bath with liquor sprays from the top will be of increasing interest, as they have very low liquor requirements. PIROGA/HT of Flainox (described earlier under



8.32 Electric Dyeing (Krantz and SMH).

HT softflow/overflow dyeing machines; Fig. 8.16) is one recent machine of this type giving 30% saving in water as well as 25% higher productivity.

Machines to dye fabrics in non-aqueous media will also be of increased interest. In this area Supercritical Fluid Dyeing (SFD), which does not involve a washing or drying process, will prove useful for clean dyeing of synthetic fibres. The high costs associated with equipment operating at HP and temperature (300 bar at 120°C) must be lowered in order for the use of this type of machine to become feasible; this will result in reductions in energy, water and chemical consumption as well as waste output.

In future, continuous dyeing ranges with hotflue, steamer and washing units could be developed with built-in heat and water recovery and reuse units and systems to counter pollution issues and to offer savings in terms of water and energy cost. The Venus jet dyeing machine of Sclavos, Greece (described earlier under jet dyeing machines with hydraulic flow system), has introduced a direct built-in heat recovery system and represents a pioneering step in this direction. It can also be expected that standards and statutes could be implemented in order to encourage and enforce such built-in systems for cleaner and more economic dyeing.

The above examples of developing technologies are cited in order to illustrate future trends in innovative dyeing machinery for more ecological and economical fabric dyeing. In addition to this, the current trends will continue towards improved safety standards, greater operational ease and accuracy through automation at all stages, and the management of complete dyeing operations, with the aim of achieving maximum efficiency in machine operations and dyeing processes (Websites of Machinery Manufacturers, 2005, 2008, 2009).

In short, dyeing machines will be developed in the future that can achieve minimum consumption of resources and minimum generation of effluents while producing dyed textiles of excellent quality at competitive prices.

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### 8.13 Appendix: list of machinery manufacturers

ACME	ACME Machinery Industry, Taiwan	(website not available)
AKM	Asia Kingdom Machinery, Taiwan	www.akdyeing.com
Alkan Alliance	Alkan Makina, Turkey Alliance Machines Textiles, France	www.alkanmakina.com www.alliance-mb.com
Anjani	Anjani Industries, Surat, India	www.anjaniindustries.com
ATYC	Argelich Termes Y Cia, Spain	www.atyc.es
Barco	Barco, Belgium	www.barco.com/textiles
Bellini	Loris Bellini, Italy	www.loribellini.com
Benninger	Benninger, Switzerland	www.benningergroup.com
Brazzoli	Brazzoli, Italy	www.brazzoli.it
Brückner	Brückner Trockentechnik, Germany	www.brueckner-tm.de
Brugman	Brugman, Holland, Netherlands	www.Brugman-holland.nl
Canlar Makina	Canlar Makina San. Tic., Turkey	www.Canlarmakina.com
Dalal	Dalal Engineering, Mumbai, India	www.dalalengineerinf.com
Devrekha	Devrekha, Surat, India	www.devrekha.com
Dhall	Dhall Enterprises & Engineers, Ahmedabad, India	www.dhallenginerring.com
Dilmenler	Dilmenler Makina, Turkey	www.dlmenler.com.tr

Embee	Embee Corporation, Ahmedabad, India	<a href="http://www.embeeindia.com">www.embeeindia.com</a>
Erbatech	Erbatech, Germany	<a href="http://www.erbatech.de">www.erbatech.de</a>
Flainox	Flainox, Italy	<a href="http://www.flainox.com">www.flainox.com</a>
Fleissner	Fleissner, Germany	<a href="http://www.fleissner.de">www.fleissner.de</a>
Fong's	Fong's National Engineering, Hong Kong-China	<a href="http://www.fongs.com">www.fongs.com</a>
Goller	Goller Textilmaschinen, Germany	<a href="http://www.goller.de">www.goller.de</a>
Harish	Harish Enterprise, Mumbai, India	<a href="http://www.harishenterprise.com">www.harishenterprise.com</a>
Henriksen	Vald. Henriksen, Netherlands	<a href="http://www.henriksen.nl">www.henriksen.nl</a>
Hisaka	Hisaka Works, Japan	<a href="http://www.hisaka.co.jp">www.hisaka.co.jp</a>
HTP Unitex	HTP Unitex, Italy	<a href="http://www.htpunitex.com">www.htpunitex.com</a>
Infab	Infab Tex-Machines, India	(website not available)
Krantz	Moenus Textilmaschinen, Germany	<a href="http://www.moenus-krantz.com">www.moenus-krantz.com</a>
Küsters	Küsters Textile, Germany	<a href="http://www.kuesters-textile.com">www.kuesters-textile.com</a>
Küsters Calico	Küsters Calico, Vadodara, India	<a href="http://www.kuesters-calico.com">www.kuesters-calico.com</a>
Lababidico	Lababidi Company, syria	<a href="http://www.lababidico.com">www.lababidico.com</a>
Laip	L.A.I.P., Italy	<a href="http://www.laip.it">www.laip.it</a>
MCS	MCS Dyeing and Finishing, Italy	<a href="http://www.mcsgroup.it">www.mcsgroup.it</a>
Metal Working	Metal Working, Brazil	<a href="http://www.metalworking.com.br">www.metalworking.com.br</a>
Mezzer	Mezzer HTP Unitex, Italy	<a href="http://www.htpunitex.com">www.htpunitex.com</a>
Minox	Minox, Italy	<a href="http://www.minox.it">www.minox.it</a>
Monforts	A. Monforts Textilmaschinen, Germany	<a href="http://www.monforts.de">www.monforts.de</a>
Morrison	Morrison textile Machinery, USA	<a href="http://www.morrisontexmach.com">www.morrisontexmach.com</a>
Nosed	Nosed, Italy	<a href="http://www.nosed1893.it">www.nosed1893.it</a>
Obem	Obem, Italy	<a href="http://www.obem.com">www.obem.com</a>
Otto Funke	Otto Funke, Germany	<a href="http://www.funkejigger.com">www.funkejigger.com</a>
Otto Pricken	Otto-Pricken, Germany	<a href="http://www.op-vh.com">www.op-vh.com</a>
PMM	Paslanmaz Malzeme Mamulleri, Turkey	<a href="http://www.pmm.tr">www.pmm.tr</a>
Pozzi	Pozzi Leopoldo, Italy	<a href="http://www.pozzi.it">www.pozzi.it</a>
Proses	Proses Makina, Turkey	<a href="http://www.prosesmakina.com">www.prosesmakina.com</a>
Reisky- Dhall	Reisky Máquinas, Brazil	<a href="http://www.reisky.com.br">www.reisky.com.br</a>
Sclavos	Sclavos, Greece	<a href="http://www.sclavos.gr">www.sclavos.gr</a>
Setex	Setex Schermuly Textile Computer, Germany	<a href="http://www.setex-germany.com">www.setex-germany.com</a>

SMH	Sucker-Muller-Hacoba (Moenus Group), Germany	<a href="http://www.moenus-sucker.com">www.moenus-sucker.com</a>
Swastik	Swastik Textile Engineers, Ahmedabad, India	<a href="http://www.swastiktextile.com">www.swastiktextile.com</a>
TEPA	Exclusivas, Te-Pa, Spain	<a href="http://www.tepa.es">www.tepa.es</a>
Tong Geng	Tong Geng Enterprises, Taiwan	(website not available)
Texlink	Texlink-China	<a href="http://www.texlinkmachine.com">www.texlinkmachine.com</a>
Tekst	Text Makina Elektronik, Turkey	<a href="http://www.tekst.com.tr">www.tekst.com.tr</a>
Makina		
Then	Then Maschinen, Germany	<a href="http://www.then.de">www.then.de</a>
Thies	Thies, Germany	<a href="http://www.thiestextilmaschinen.de">www.thiestextilmaschinen.de</a>
Yamuna	Yamuna Machine Works, Vapi, India	<a href="http://www.yamunamachine.com">www.yamunamachine.com</a>

## The chemistry of reactive dyes and their application processes

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**Abstract:** Reactive dyes have proven to be one of the most successful classes of modern synthetic dyes. The reasons for this success lie in their shade versatility, their flexibility in application and the all-round good fastness properties obtained from dyeings produced with reactive dyes on wool, silk, cotton and regenerated cellulosic fibres. The chemistry of the different reactive groups used, the chemistry of reactive dye manufacture and the chemical principles behind their application to cellulosic fibres and polyamide fibres are reviewed.

**Key words:** reactive dyes, development history, chemistry of reactive groups, multi-functional reactive dyes, application to cellulosic fibres, nucleophilic sites, substantivity effects, application to natural and synthetic polyamide fibres, fibre modification to enhance fixation, cross-linking to covalently fix dyes on fibres.

### 9.1 Introduction

Reactive dyes may be loosely defined as chromophores which contain pendant groups capable of forming covalent bonds with nucleophilic sites in fibrous substrates. Providing these covalent bonds are stable to conditions encountered in laundering, the wash-fastness properties of the colourations will be outstanding. Unlike other dye classes used on cellulosic substrates, the reactive dyes cover a very wide shade gamut from black to vibrant brilliant shades, accounting for their early commercial success in this area.

Reactive dyes have also become more widely used on polyamide materials as a means to produce dyeings and prints of excellent wash-fastness; additionally in the case of wool they exhibit a fibre protective effect which diminishes damage in dyeing and are also seen as alternatives to chrome dyes.

In addition to the detailed descriptions given in this chapter the reader is referred to very useful texts on reactive dyes and their application.<sup>1-7</sup>

## 9.2 The history of reactive dye development

### 9.2.1 Earliest attempts to covalently bond dyes to textile substrates

The pioneering work of Cross and Bevan<sup>8</sup> was probably the first attempt to produce a dye–fibre covalent bond and thus achieve dyeings of very high wet-fastness. These early studies were directed at producing a covalently bonded colour on cellulosic fibre substrates, the driving force clearly coming from the very modest wet-fastness properties of colourations produced with direct dyes on cotton and viscose. Significant early research was also carried out to covalently attach dye chromophores to wool but there was little urgency to market such products since wool fibres could be dyed to reasonably high fastness standards using chrome mordant dyes.

Cross and Bevan<sup>8</sup> pre-treated cotton with benzoyl chloride, nitrated the benzoyl ester, reduced the nitro groups to amines, diazotised the amine residues and coupled them to 2-naphthol, producing an orange colouration that was resistant to very severe washing conditions; this chemistry is summarised in Fig. 9.1. This six-step process was highly impractical, especially viewed in the modern reactive dye application context, but it did confirm the excellence of the wet-fastness achievable from such covalently bonded colourations.

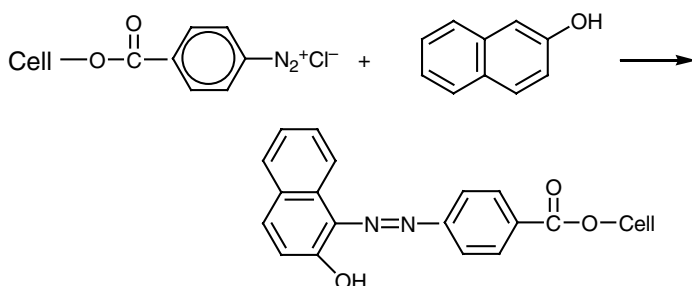
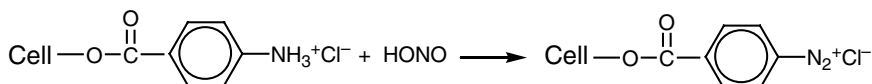
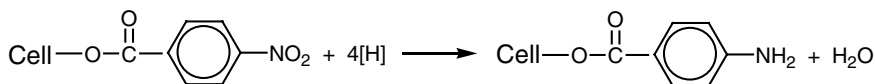
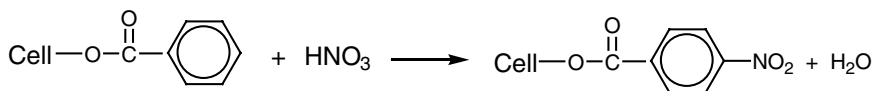
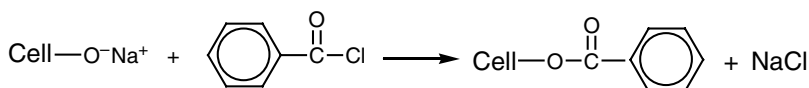
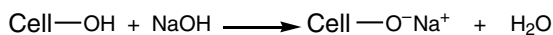
In 1930 Haller and Heckendorn<sup>9</sup> at Ciba dissolved cyanuric chloride in xylene and reacted this solution with ‘alkali’ cellulose to produce an electrophilic fibre, 2,4-dichloro-*s*-triazinyl-O-cellulose, which would react with water-soluble dyes containing a pendant amino group, to give dyeings of high wet-fastness.

### 9.2.2 Early wool reactive dyes

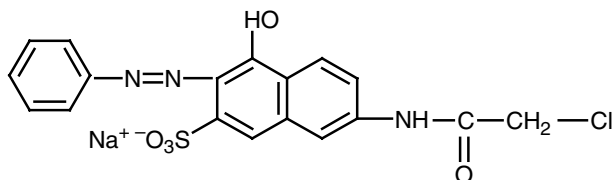
In the 1930s Clingenstein and IG Farben<sup>10</sup> patented chloroacetylamino dyes for wool and subsequently IG marketed Supramino Orange R as an acid dye for dyeing wool under mildly acidic conditions. This dye contained a pendant  $\omega$ -chloroacetylamino side-chain – the dye had the structure shown in Fig. 9.2.

When comparing wool dyeings produced with this chloroacetyl dye and the acetate analogue, the very good wet-fastness properties of the former dyeings were attributed, at this time, to the increased molecular mass of the chloroacetyl dye rather than to dye–fibre covalent bonding.

In 1949 Heyna and Schuhmacher<sup>11,12</sup> and the Hoechst Company patented dyes which gave wool dyeings of excellent wash-fastness – the Remalan



9.1 The Cross and Bevan procedure for covalent bonding a colourant to cotton cellulose.



9.2 Supramino Orange R (IG Farben).

Fast dyes. These dyes contained a  $\beta$ -sulphatoethylsulphone side-chain. It is unlikely that the patentees did not realise that these were in fact reactive dyes and one may conclude that the sales division of the company did not wish this fact to be common currency. This ground-breaking work was recognised in 2000 by the posthumous award of the Society of Dyers and Colourists' Perkin Medal to both Heyna and Schuhmacher.

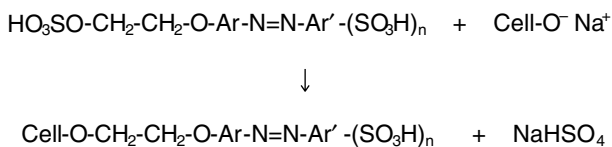
### 9.2.3 Early cotton reactive dyes

Guthrie<sup>13</sup> published an important paper in 1952 showing that a sulphatoethoxyphenylazo dye could be applied and covalently fixed on cotton by an alkaline pad-dry-bake process to give dyeings of good wash-fastness. Some of these dyes were only made water soluble by the pendant sulphato group; thus the fixation process produced a mixture of covalently bonded dye and water-insoluble pigment; the latter was not readily removed by a soaping procedure and was the source of poor rub-fastness properties of the dyeings especially in deep shades. However, some of the dyes did contain sulphonate groups directly attached to the chromophore (e.g. the bluish-red dye prepared by diazotising 2-(*p*-aminophenoxy)ethylsulphuric acid and coupling the diazo salt to 1,8-dihydroxy-naphthalene-3,6-disulphonic acid). This work deserves greater acclaim than it has received since it was the first time that good wash-fast dyeings had been achieved on cotton fabric using a preformed water-soluble chromophore containing a pendant reactive group. The reactions carried out are summarised in Fig. 9.3.

The above workers also found that the pendant sulphato group could be replaced with chlorine to give dyes which would covalently bind to cotton under alkaline pad-bake application conditions.

In 1956, following work by Rattee and Stephen,<sup>14</sup> the first range of fully water-soluble reactive dyes for cellulosic fibres was launched by ICI and named Procion MX; these workers were subsequently awarded the Perkin medal of the Society of Dyers and Colourists for the development of commercially viable reactive dyes for cotton.

Patenting new reactive dye systems then became intensive as other major dye manufacturing companies rushed to get into this promising area. Dyes containing monochloro-*s*-triazine residues (MCT dyes) had already been patented and marketed by Ciba in the late 1920s as direct dyes for cellulose fibres although their potential to react covalently with cotton had not been exploited; it is thus not surprising that ICI and Ciba made an agreement in 1957 to respectively market Procion H and Cibacron MCT dyes. Geigy and Sandoz developed the less activated pyrimidine ring system (compared



Where Ar and Ar' represent different substituted aromatic moieties

9.3 The covalent fixation of a sulphatoethoxyphenylazo dye on cotton.



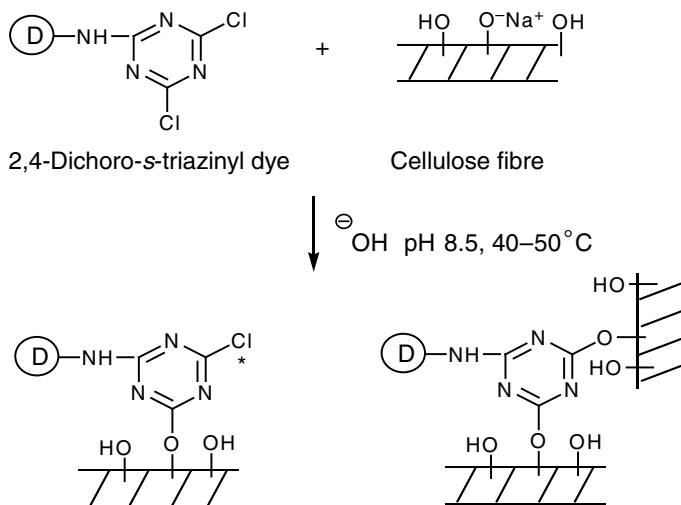
to triazine) and launched 2,4,5-trichloropyrimidine dyes in 1959. Bayer invented the 2,3-dichloroquinoxaline Levafix E dyes and marketed them in 1961. Hoechst revisited their Remalan Fast wool dye range mentioned earlier and quickly devised application conditions making the vinylsulphone dyes suitable for cellulose fibre colouration, thus launching the very successful Remazol range of dyes in 1957.

In all the above the major drive was to develop a wide shade gamut of chromophoric molecules applicable to cellulose giving colourations of good wash-fastness; thus wool, where much of the reactive dye innovation started, was temporarily side-lined. There is no doubt that reactive dyes have been a major success for cellulose fibres; 130 000 tonnes of reactive dye were sold in the year 2000 for the colouration of cotton and regenerated cellulosic fibres, which represented 38% of the cellulose fibre dye market of 339 000 tonnes.<sup>15</sup> However with pressure on the use of heavy metals in wool dyeing there is currently a strong trend developing to use reactive dyes to a greater extent on wool and other polyamide fibres. Thus the Lanazol ( $\alpha$ -bromoacrylamido) dyes, introduced by Ciba in 1966, have become widely used on wool fibres and, to a lesser extent, vinylsulphone and 2,4-difluoro-5-chloropyrimidine (FCP) dyes are also being used on wool and other polyamide fibres.

### 9.3 Chemistry of commercially available reactive dyes

#### 9.3.1 Halo-triazines

The early work at ICI established that dichloro-*s*-triazine (DCT) dyes could be cheaply synthesised by the reaction of so-called amino dye bases (Chromophore-NH<sub>2</sub>) with cyanuric chloride, a material which was already available in large tonnages from their agro-chemical division. The DCT dyes could be applied to cellulosic substrates by long-liquor (exhaust) dyeing procedures and by a variety of pad-fixation processes. In long-liquor dyeing these dyes were absorbed by the substrate, firstly in the presence of electrolyte and secondly in the presence of added alkali. It was a surprise that even under mild alkaline conditions (pH 8.0–9.0, 40°C) used in this second phase, the dyes underwent efficient covalent bonding or *fixation* with cellulose hydroxyl groups. Initially it seemed that this development might remain a laboratory curiosity, since the storage stability of these new dyes was poor due to moisture sorption and subsequent acid catalysed hydrolysis to form the inactive di-hydroxy-*s*-triazine derivative; ICI scientists overcame this problem by dry mixing the dye powder with solid sodium dihydrogen phosphate and sodium hydrogen phosphate buffer. Horrobin<sup>16</sup> has very adequately described the hydrolysis chemistry of these dyes. Figure 9.4 summarises the basic chemical principles of the DCT dye reaction with cellulose and the competing hydrolysis reactions.



\* A Type III dye-fiber bond is formed by the alkaline hydrolysis of the Type I system (thus replacing chlorine with hydroxyl)

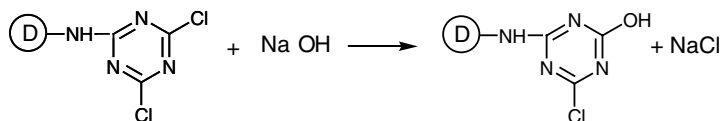
(D) represents a sulphonated chromophore

9.4 The dye-fibre fixation process for a dichloro-*s*-triazine dye on cellulosic fibres.

Referring to Fig. 9.4, the mono-chloro-*s*-triazine-O-cellulose monoester (Type I) and the di-ester (Type II) dye-fibre bonds have good stability to washing, but the mono-hydroxy-*s*-triazine-O-cellulose (Type III) bond shows poor acid stability; hence dyed goods which originally show excellent wet-fastness properties may show a deterioration of these properties on storage due to uptake of acid fumes promoting conversion of Type I bonds to Type III bonds.

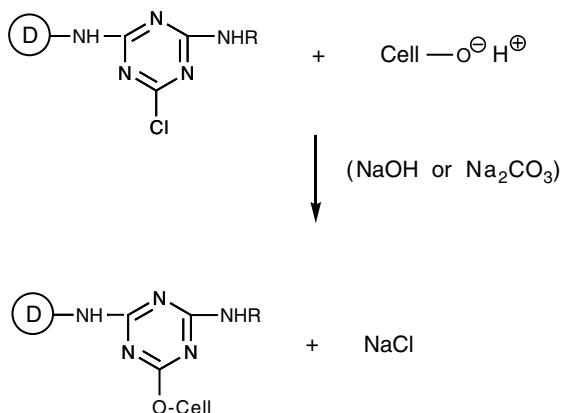
The reactions of DCT dyes with cellulose are classical  $\text{S}_{\text{N}}2$  bimolecular substitution reactions resulting from nucleophilic attack of the electron-rich oxygen in the cellulosate anion on electron deficient carbon atoms in the triazine heterocycle. Chloride anion is the leaving group in these reactions.

One of the major problems which adversely affects the efficiency of reaction with the cellulosate anions in the fibre is the presence of nucleophilic hydroxyl anions present in the alkaline solution used in the fixation phase – these also react with the DCT residue in the dye to give the monochloro-monohydroxy-*s*-triazine dye (Fig. 9.5).



Where (D) represents a sulphonated chromophore

9.5 The competing hydrolysis reaction for DCT dyes.



Where (D) represents a sulphonated chromophore

9.6 The reaction of monochloro-monoamino-triazine dyes with cotton cellulose.

Under alkaline conditions, the reaction stops at the monochloro-mono-hydroxy-*s*-triazine stage since the triazinyl hydroxy group is deprotonated (phenolate character) and the electron-rich cyanurate oxygen essentially feeds electrons back into the heterocyclic ring and deactivates the carbon atom (attached to the remaining chlorine) towards further nucleophilic substitution.

When cotton printers tried to use the new DCT dyes for printing, it was quickly realised that their stability in water-based printing pastes was too low – printers need to store such pastes at least 24 h; thus the deactivated monochloro-monoamino-*s*-triazine (MCT) dyes were developed (Procion H – now Procion P dyes). To achieve dye–cellulose covalent bonding such reactive dyes required more severe application conditions than DCT dyes, such as increased alkalinity and higher temperature. Figure 9.6 summarises the reaction of these dyes with cellulosic fibres.

Although developed for printing the MCT dyes are also widely used in long-liquor dyeing processes since they can be designed to exhibit high substantivity for the cellulose fibre; they are applied at 80°C first in the presence of electrolyte and then, in the second stage, fixed by the addition of sodium carbonate, in contrast to the 40°C application conditions recommended for the DCT dyes.

Cyanuric fluoride was developed by Bayer in 1957 as an intermediate to produce monoamino-monofluoro-*s*-triazine (MFT) reactive dyes.<sup>17</sup> Subsequently MFTs have gained significant importance for printing and long-liquor dyeing (e.g. Cibacron F dyes from Ciba – now sold as Novacron F dyes by Huntsman). In long-liquor dyeing of cotton and viscose they are fixed at 60°C at pH 10.5–11.0 (sodium carbonate).

### 9.3.2 Halo-pyrimidines

In 1958, in response to the introduction of triazine based reactive dyes for cellulosic fibres, Geigy and Sandoz introduced 2,4,5-trichloropyrimidine dyes<sup>18</sup> and these were marketed as Reactone and Drimarene dyes respectively. The pyrimidine ring compared to triazine is much less activated towards nucleophilic substitution and thus these dyes are fixed at 95°C when exhaust dyeing cellulosic fibres. The dyes are synthesised by condensation of the amino dye base with 2,4,5,6-tetrachloropyrimidine –the latter is produced commercially in a variety of ways including chlorination of barbituric acid;<sup>19</sup> Lewis acid catalysed thermal condensation of  $\alpha$ -trichloro-isocyanide-dichloride;<sup>20</sup> chlorinating cyclisation of N-substituted 3-aminopropionitriles.<sup>21</sup>

Analogous to the fluoro-triazine system, it was discovered that fluorine substituted pyrimidines were much more reactive to nucleophiles than the chloro analogues; in particular the FCP dyes are commercially successful since in exhaustion dyeing these dyes can be fixed on cellulosic substrates at 60°C in the presence of sodium carbonate.<sup>22</sup> These 2,4-difluoro-5-chloropyrimidine (FCP) dyes are prepared by the reaction of 2,4,6-trifluoro-5-chloro-pyrimidine with an amino dye base; once again Bayer fluorination technology was used to convert the tetra-chloropyrimidine to the tri-fluoro-monochloropyrimidine and as a result Bayer and Sandoz marketed the Levafix EA and Drimarene R/K dyes respectively.

### 9.3.3 Halo-quinoxalines

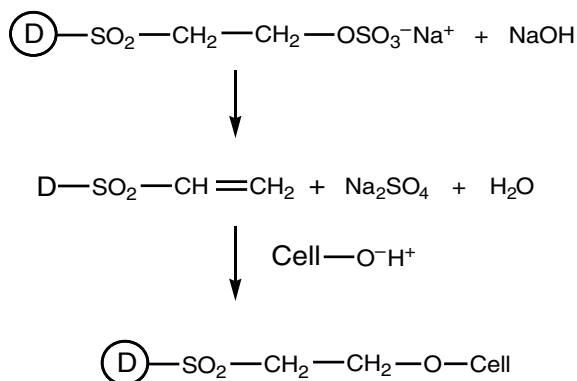
Reactive dyes which contained the 2,4-dichloro-quinoxaline (DCQ) reactive residue were developed by Bayer and marketed as Levafix E – once again they were suitable for exhaustion dyeing of cellulose at 60°C and fixed by adjusting alkalinity with sodium carbonate additions. The DCQ dyes are

synthesised by the condensation of an amino dye base with 2,3-dichloroquinoline-6-carbonyl chloride – the latter being prepared from toluene by a seven-step reaction.<sup>23</sup>

### 9.3.4 Vinylsulphone dyes

As mentioned previously, dyes containing masked vinylsulphone residues were sold by Hoechst as Remalan Fast dyes for wool; the most common masking group used in commercial dyes is a  $\beta$ -sulphato residue and occasionally a  $\beta$ -chloro residue. Following Rattee and Steven's successful application work to covalently bond halotriazine dyes on cellulosic fibres it was not surprising that Hoechst chemists evaluated the Remalan Fast dyes using similar alkaline conditions; the system functioned well giving good dye–fibre covalent fixation values on cellulosic fibres. The Remazol dye range, based on masked vinylsulphone systems, thus appeared for dyeing and printing cellulosic fibres; the masking sulphato or chloro group is removed by a 1,2-trans elimination reaction, during the dyeing process, to form the free vinylsulphone group which then reacts with fibre nucleophiles by the Michael addition reaction. Figure 9.7 describes these reactions.

There are a number of routes to prepare the masked vinylsulphone dyes and most rely on the efficient production of 4-aminophenyl- $\beta$ -sulphatoethylsulphone (*para*-base) or 3-aminophenyl- $\beta$ -sulphatoethylsulphone (*meta*-base); azo dyes (e.g. yellows, reds and oranges) are made by diazotising and coupling the above *p*- or *m*-bases to selected coupling



Where  $\textcircled{\text{D}}$  represents a sulphonated chromophore

9.7 The reactions involved when dyeing cotton cellulose with vinylsulphone reactive dyes.

components such as sulphonated naphthols; the renowned brilliant blue, anthraquinone dye, Remazol Brilliant Blue R (C.I. Reactive Blue 19) is prepared by condensing bromamine acid with *meta*-base.

Typically *para*-base, 4-aminophenyl- $\beta$ -sulphatoethylsulphone, is prepared according to the following steps: (i) reaction of acetanilide with chlorosulphonic acid to give 4-chlorosulphonyl-acetanilide; (ii) reaction of 4-chlorosulphonyl-acetanilide with sodium sulphite to give sodio 4-sulphinato-acetanilide; (iii) reaction of sodio 4-sulphinato-acetanilide with ethylene oxide to give 4-hydroxyethylsulphone-acetanilide; (iv) acid hydrolysis of 4-hydroxyethylsulphone-acetanilide to give the 4-aminophenyl- $\beta$ -hydroxyethylsulphone and (v) reaction of 4-aminophenyl- $\beta$ -hydroxyethylsulphone with concentrated sulphuric acid to give the required *p*-base, 4-aminophenyl- $\beta$ -sulphatoethylsulphone.

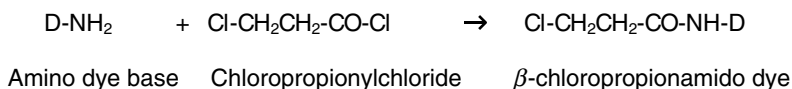
A typical route for the production of the more expensive *meta*-base is react *m*-benzenesulphonylchloride with sodium sulphite to give 3-*m*-benzenesulphinato which is then reacted with ethylene oxide to give the corresponding hydroxyethylsulphone – nitration to give 1-nitro-benzene-3-hydroxyethylsulphone, reduction of the nitro group to the amine followed by final esterification with concentrated sulphuric acid gives the required *m*-base, 3-aminophenyl- $\beta$ -sulphatoethylsulphone.

### 9.3.5 Acrylamide and substituted acrylamides

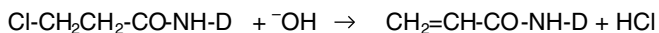
The early Primazin (BASF) reactive dyes for cotton contained the  $\beta$ -chloropropionamido group attached to a chromophore; during alkaline application HCl was eliminated and an acrylamido-dye was formed; Michael addition of the activated double bond to Cell-O<sup>-</sup> under alkaline conditions resulted in covalent dye–fibre bond formation. The preparation of these dyes and their reaction with cotton cellulose are summarised in Figs. 9.8 and 9.9 respectively.

These dyes were not on the cotton dyeing market for very long, probably due to the amido group in the dye–fibre bond being susceptible to alkaline hydrolysis during laundering. However, reactive dyes containing this reactive group were used extensively for wool dyeing.

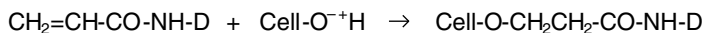
The most successful reactive dyes for wool dyeing are the Lanazol<sup>24,25</sup> dyes originally marketed by CIBA but now Huntsman; these are  $\alpha$ -bromoacrylamido dyes prepared as shown in Fig. 9.10.



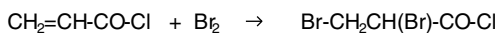
9.8 Preparation of  $\beta$ -chloropropionamido dye.



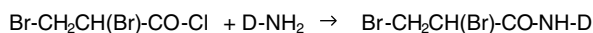
## Acrylamido dye



9.9 Alkaline fixation of  $\beta$ -chloropropionamido dye to cellulosic substrate.



Acryloyl chloride                      2,3-Dibromopropionylchloride



2,3-Dibromopropionamido dye



$\alpha$ -Bromoacrylamido dye

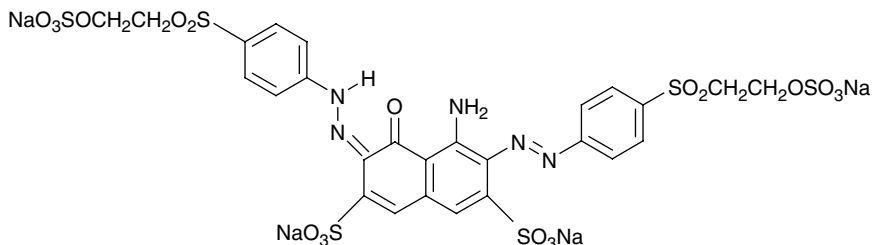
9.10 Preparation of Lanazol  $\alpha$ -bromoacrylamido dyes.

### 9.3.6 Polyfunctional reactive dyes

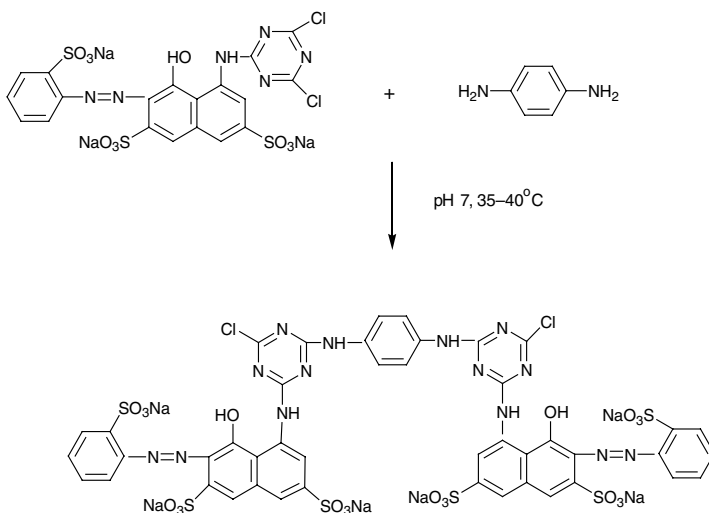
Polyfunctional reactive dyes were already represented in one of the earliest classes of reactive dye introduced for cotton dyeing, the DCT dyes; these dyes contained two reactive sites but the likelihood of actually achieving two dye–fibre bonds with cellulose hydroxyl residues is quite low due to the competing hydrolysis reaction. The first efficient bifunctional dye was the Hoechst product, Remazol Black B (C.I. Reactive Black 5), which was marketed in 1957 as part of the original Remazol range; this dye is now by far the biggest selling dye in the world being used for producing navy blue and black shades on wool, cotton and viscose. The structure of this dye is shown in Fig. 9.11.

In cold pad-batch applications, C.I. Reactive Black 5 is capable of giving total fixation values greater than 90% in moderate depths of shade; in long-liquor applications it gives total fixation values of the order of 70% due to its only moderate substantivity.

In the early 1970s ICI developed an elegant, cheap, highly practical method to prepare homo-bifunctional dyes by simply reacting two moles of a DCT dye with one mole of a diamine such as *p*-phenylene diamine to give a bis-MCT



9.11 C.I. Reactive Black 5.

9.12 Preparation of a typical bis-monochloro-*s*-triazine dye.

dye; in this way the technically important Procion HE range of reactive dyes was developed. A typical synthetic route to the manufacture of the bis-MCT dye, Procion Red HE-3B (C.I. Reactive Red 120), is shown in Fig. 9.12.

In the mid-1990s Ciba launched Cibacron LS bifunctional dyes based on bis-MFTs; these dyes were prepared from the condensation of two moles of di-fluoro-triazine dye with a suitable diamine (e.g.  $\alpha$ ,  $\omega$ -diamino-propane). These dyes were of such a molecular size as to be highly substantive to cellulose and thus could be dyed in the presence of reduced salt, e.g. 40 g/L sodium sulphate – hence the use of the LS suffix (Low-Salt). The MFTs are significantly more reactive than the monochlorotriazine dyes and are thus fixed on cotton at pH 10.5–11.0 at 60°C rather than 80°C. The high

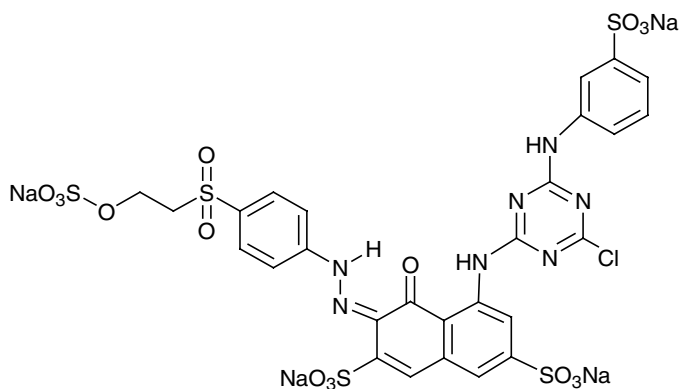


substantivity of these dyes leads to unlevel dyeings in dyeing machines with low rates of fibre–liquor interchange.

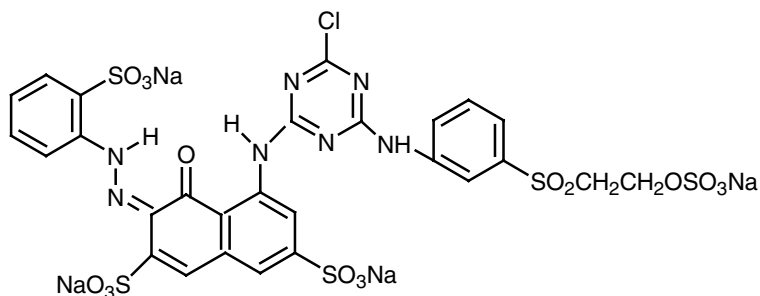
In 1980 Sumitomo launched the first complete range of hetero-bifunctional reactive dyes which contained both a monochlorotriazine and a sulphatoethylsulphone group attached to the same dye molecule; these were named Sumifix Supra. This concept was not entirely novel; Hoechst already had one or two similar dyes in their Remazol range – for example Remazol Red RB has the structure shown in Fig. 9.13.

An important difference in the Sumifix Supra range of dyes was the fact that all were prepared by the condensation of a parent DCT dye with *m*-base, 1-aminobenzene-3-sulphatoethylsulphone. It was claimed by Sumitomo<sup>26</sup> that the use of *m*-base, rather than the cheaper *p*-base, allowed the creation of a range of dyes which were of high compatibility in mixture shades; this is because corresponding *p*-base dyes show wider variations in individual dye reactivity. As well as being of high combinability these dyes, when dyed on cellulosic substrates in the temperature range 60–80°C, gave repeatable fixation values; thus if there were temperature variations from front to back of a dyeing machine, shade reproducibility would not be compromised. A typical structure of a Sumifix Supra dye is shown in Fig. 9.14.

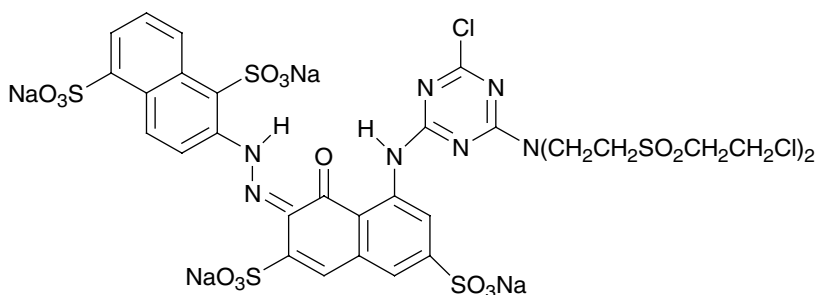
The concept of hetero-bifunctionality has been further developed commercially by Ciba (now Huntsman) with their Cibacron C (now Novacron C) dyes designed particularly for pad-batch application; many of these dyes were based on the reactive 2-vinylsulphonylethylamino-4-fluoro-s-triazine residue. In this case the reactive electrophilic groups in the dyes were designed to be of similar reactivity; having the reactive vinylsulphone residue attached through an aliphatic amine to triazine imparted flexibility to the reactive group which increased the likelihood of reaction with the cellulose anions; in addition aliphatic vinylsulphone-alkylamine-triazine



9.13 Remazol Red RB.



9.14 Sumifix Supra Brilliant Red 2BF.



9.15 Remazol Red SBB.

residues improved the water solubility of the dye compared with analogous dyes containing aromatic vinylsulphone-arylamine-triazine residues.

The halo-pyrimidine-based dyes may also be viewed as hetero-bifunctional since each dye contains at least two halogen leaving groups; these carbon-halogen sites are selectively activated because the pyrimidine ring is asymmetric; thus in the case of FCP dyes the 4-fluoro carbon site is most reactive, reacting with cellulose in the presence of sodium carbonate at 60°C; for the 2-fluoro carbon electrophile to react efficiently with cellulose a temperature increase of some 10°C would be required.

Tri-functional dyes have been developed and when applied to cotton in long-liquor dyeing processes are capable of fixation efficiencies approaching 90% in medium depths of shade. Thus Everlight have a tri-functional range (Everzol ED) and it is believed that some of the Procion HE-XL+ dyes are tris-monochloro-triazines; the latter may be prepared by the reaction of three moles of a DCT dye with one mole of a tri-functional amine. As early as 1975 Hoechst launched the tri-functional dye, Remazol Red SBB (C.I. Reactive Red181) which is shown in Fig. 9.15; Hoechst also patented dyes of this type.<sup>27</sup>

It is interesting that tetra-functional reactive dyes have not, as yet, been prepared by replacement of the residual MCT in Fig. 9.15 with a further mole of bis-chloroethylsulphone-ethylamine; the problem lies in the conditions required (pH 8.0–9.0, 80–90°C) which lead to vinylsulphone formation and this vinylsulphone quickly reacts with the amine preventing its condensation with the chloro-triazine. Less reactive vinylsulphone blocking groups may lead to a resolution of this problem by delaying vinylsulphone formation.

Tetra-functional reactive dyes have been claimed in the patent literature; for example Ciba have covered chromogens containing two vinylsulphone/monohalo-*s*-triazine residues.<sup>28</sup> A Proctor and Gamble patent<sup>29</sup> describes tetra-functional reactive dyes prepared from the reaction of DCT dyes (or difluoro-monochloro-pyrimidine dyes) with two moles of cysteamine and subsequent reaction of the two pendant primary amines with cyanuric chloride; the preparation route is summarised in Fig. 9.16.

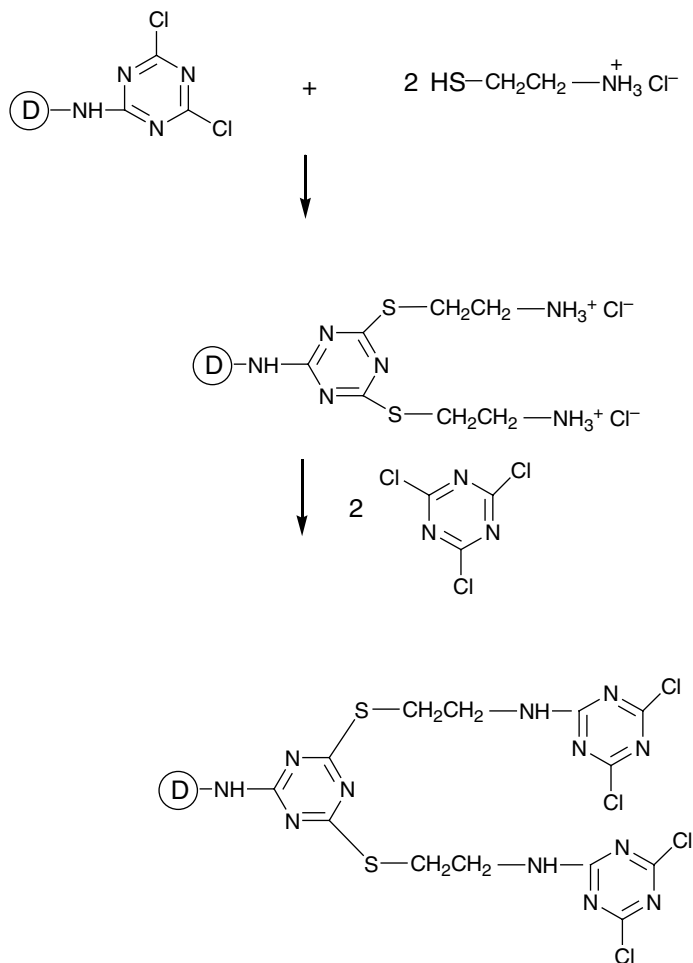
When these dyes were applied to cotton, in medium shade depths, by long-liquor processes at 50°C in the presence of 40 g/L sodium sulphate and fixed with sodium carbonate additions, total fixation efficiencies greater than 95% were obtained; in addition the large hydrophobic side-chain gave the dyes very good combinability properties in tertiary shades. The dyes were also applicable by pad-batch processes but in this case it was preferable to replace the cysteamine bridging group with cysteine in order to enhance water solubility of the dyes.

Morris *et al.*<sup>30</sup> replaced cysteamine with ethylene-diamine to produce related tetra-functional reactive dyes; in the following example one mole of the starting DCT dye, C.I. Reactive Red 1, was reacted with two moles of ethylene-diamine to give the bis-ethylene-diamine intermediate shown in Fig. 9.17.

The diamine intermediate (1 mole) shown in Fig. 9.17 was reacted with two moles of cyanuric chloride at 0–5°C at pH 10 to give the required tetra-chloro-*s*-triazine (bis-DCT) dye (Fig. 9.18) which was isolated at pH 6.0.

The improved efficiency of the tetra-chloro-*s*-triazine dye (bis-DCT) versus the starting DCT, when applied in long-liquor dyeing (60°C and fixation at pH 10.5) at 2% o.m.f. depth, is shown in Fig. 9.19 (o.m.f. is the abbreviation for 'on mass of fibre'). The bis-DCT dye gave a total fixation efficiency value (T) of 93% whereas the parent DCT dye gave a T value of 69%.

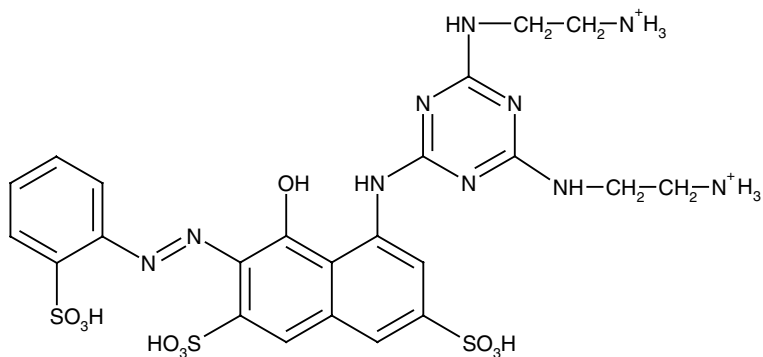
In the initial neutral exhaustion phase, it can be seen that the two dyes exhausted at a similar rate. Little absorbed dye fixation occurred for the bis-DCT dye during this stage; however, the parent DCT dye exhibited significant levels of absorbed dye fixation due to the highly reactive nature of the DCT group when attached as in the parent dye. The lower neutral reactivity of the bis-DCT dye is advantageous as it allows greater control of the absorption phase and thus leads to better level dyeing properties.



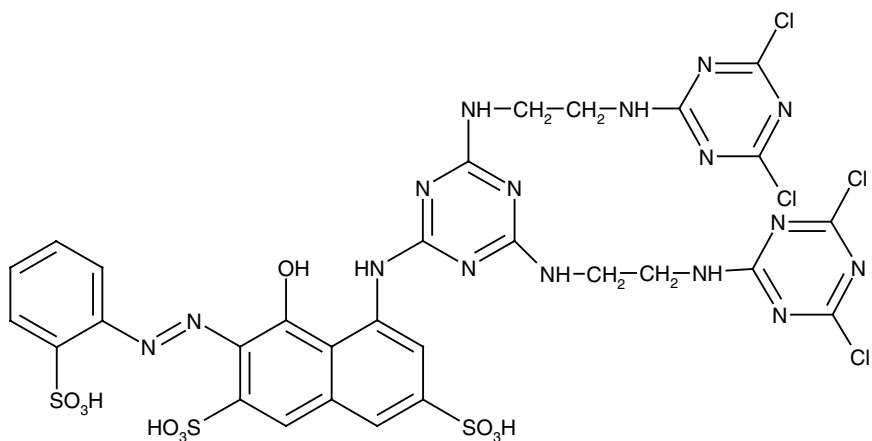
Where  $\textcircled{\text{D}}$  is a sulphonated chromophore

#### 9.16 Synthesis of a tetra-functional chloro-s-triazine dye.

The differences in the exhaustion/fixation profiles of the bis-DCT dye and the DCT dye may be seen further into the fixation phase – post alkali addition. The bis-DCT dye underwent rapid fixation during the first 5 min after the addition of the alkali, after which time the rate of fixation slowed down but still continued to increase. In comparison, this was different from the trend seen for the parent DCT dye where no additional increase in the level of absorbed dye fixation was seen above that already achieved during



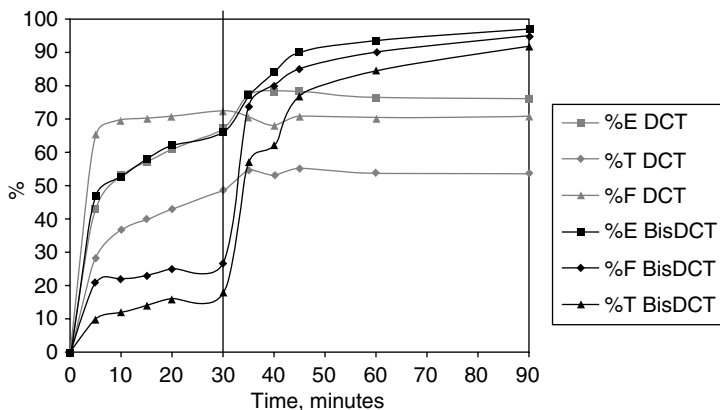
9.17 Bis-ethylene-diamine intermediate.

9.18 Tetra-chloro-*s*-triazine dye from C.I. Reactive Red 1.

the neutral exhaustion phase. The convergence of the exhaustion, absorbed dye fixation and total dyeing fixation efficiency curves associated with the new bis-DCT dye would appear possible, whereas the corresponding curves for the DCT dye run parallel with each other, showing no such convergence when increasing the length of time of dyeing.

When applying the DCT and new bis-DCT dyes (2% depth) by a pad-batch technique in the presence of sodium carbonate, the maximum level of covalent dye fixation observed with the DCT dye was 74% whereas with the bis-DCT dye the corresponding value was 96%.

Dyeings produced from the bis-DCT and DCT dyes were boiled in dilute acetic acid solution (pH 3); the dye-fibre bond generated from the



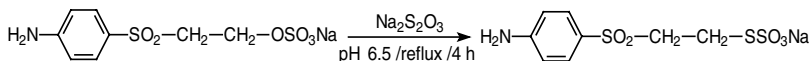
9.19 Comparison of the exhaustion/fixation profiles of the DCT dye and the bis-dichlorotriazine (bis-DCT) dye – 20 g/L sodium carbonate added after 30 min dyeing.

DCT reactive dye was very susceptible to cleavage since the acid solution became very coloured whereas no colour desorbed into the acid solution in the case of bis-DCT dyed samples. The increased dye–fibre bond stability achieved with the new bis-DCT dye is conferred by the aliphatic bridging group which deactivates the triazine ring system. The amino bridging group found in the DCT dye and many other commercially available reactive dyes, based on reactive heterocycles, is such that the triazine is linked directly to the aromatic chromophore which results in a more activated triazine system giving a dye–fibre bond prone to acid hydrolysis.

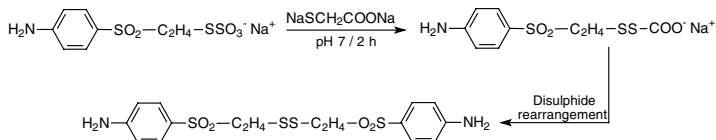
Lewis *et al.*<sup>31,32</sup> investigated the use of the disulphide-bis-ethylsulphone group to link two identical chromophores and showed these dyes had good substantivity and would covalently fix to cotton following elimination to the single vinylsulphone moieties. The starting intermediate was prepared from the reaction of *p*-base with sodium thiosulphate to form the Bunte Salt, which was then converted to the symmetrical disulphide by reaction with sodium thioglycollate (Figs. 9.20–9.22). The performance of this type of dye was much improved by preparing hetero-bi-functional analogues<sup>33</sup>, using the reactions outlined in Figs. 9.23–9.25.

### 9.3.7 Neutral fixing reactive dyes for cellulosic fibres

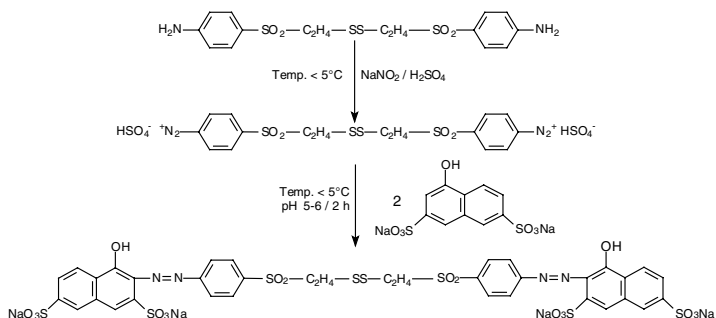
Nippon Kayaku introduced the first range of ‘neutral-fixable’ reactive dyes for cellulosic fibres in 1983; these dyes were bifunctional bis-nicotinoyl-*s*-triazines.<sup>34</sup> The chemistry behind this range of dyes was based on an early observation that the reactivity of MCT dyes could be greatly enhanced by dyeing in the presence of tertiary amines;<sup>35</sup> thus alkaline fixation at 50°C



9.20 The synthesis of 1-aminobenzene-4-s-thiosulphatoethylsulphone (Bunte salt).



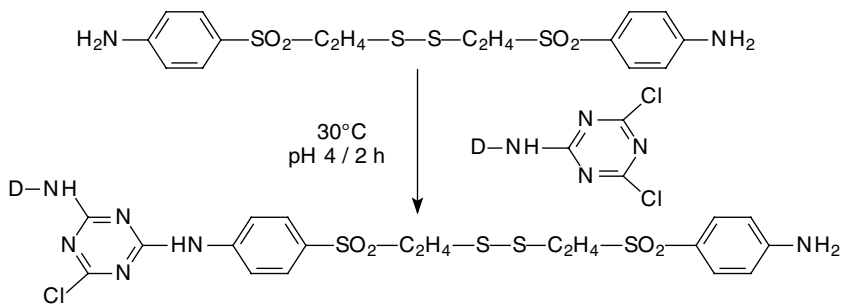
9.21 The synthesis of disulphide-bis-ethylsulphone diamine intermediate.



9.22 The synthesis of a disulphide-bis-ethylsulphone (DSBES) dye.

rather than 80°C was possible in long-liquor dyeing processes. Subsequently catalytic quantities of tertiary amines such as diazabicyclo-octane (DABCO) were promoted as dyebath additives to convert hot dyeing systems to warm dyeing systems; a good example was Cibacron Catalyst CC1 from Ciba. The procedure did not develop as rapidly as expected probably because of the odour and toxicity problems of certain tertiary amines. In 1979 ICI launched Procion Blue HE-G (C.I. Reactive Blue 187) which was prepared by reaction of a bis-MCT dye with nicotinic acid; the structure of this dye is shown in Fig. 9.26.

The use of nicotinic acid as a low toxicity, non-odorous tertiary amine attracted the interest of Nippon Kayaku researchers who made the novel observation that simply applying these dyes in boiling baths containing usual amounts of electrolyte along with a pH 7.5 buffer, achieved dye uptake and fixation; for deep shades it was recommended that fixation temperature

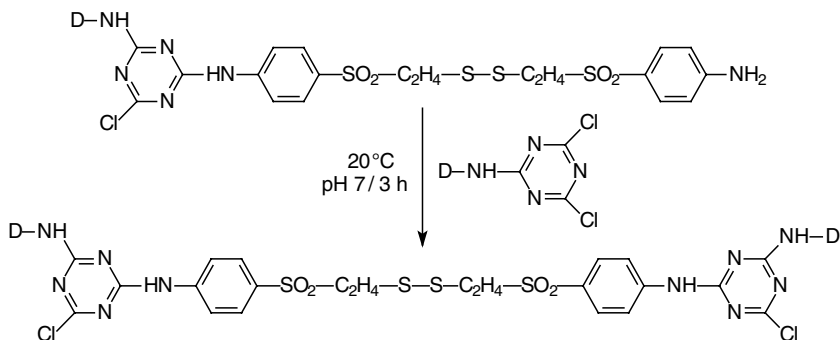


9.23 Synthesis of MCT/DSBESA intermediate.

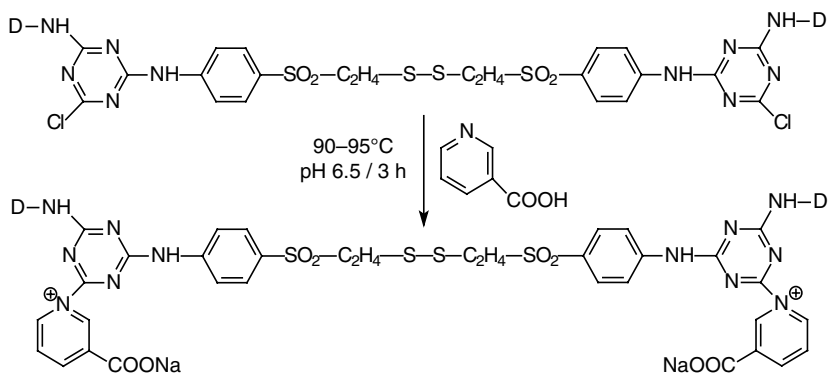
should be increased to 130°C. Croft *et al.*<sup>36</sup> investigated this concept in depth, deriving various quaternised dyes from the respective reactions of the bis-monochlorotriazine dye, Procion Red HE-3B, with nicotinic acid, DABCO, iso-nicotinic acid, nicotinamide, trimethylamine and pyridine; the reactions were carried out at pH 6.5 for 2–3 h at 80–90°C. All of these dyes showed good exhaustion and fixation values after dyeing at pH 7.0 at the boil for 1 h (e.g. for 2% shades 80–85% exhaustion and relative fixation of 70%). The concept of neutral fixation is of great interest since it simplifies the dyeing process – there is no separate fixation stage thus eliminating the need to make additions of alkali 30 min into the dyeing cycle. Hydroxyl groups in cellulose behave as very weak acids having estimated pKa values of approximately 13 at room temperature; as the temperature increases so does the dissociation and hence the nucleophilicity of the substrate. Even at the boil at pH 7.5 the number of dissociated hydroxyl groups will be very small and other reasons must be sought to explain the vastly improved fixation efficiency of quaternised triazines compared to halo-triazines. Chlorine or fluorine heterocycle-based reactive dyes produce hydrochloric or hydrofluoric acids following reaction with dissociated cellulose hydroxyl groups, but in the case of quaternised dyes the neutral haloacid salt of the tertiary amine is the leaving group. Additionally the quaternised dyes carry a positive charge adjacent to the electrophilic site which may orientate the reactive system to promote ready reaction with the negatively charged nucleophile, the cellulose anion; Fig. 9.27 shows this effect.

Vo *et al.*<sup>37, 38</sup> studied the neutral fixation of a variety of reactive dyes and confirmed that dyeing at a sufficiently high temperature would ionise sufficient Cell-OH groups to facilitate covalent reaction with the dye. Thus bis-MFT dyes and vinylsulphone dyes gave very promising fixation efficiency values when dyed at pH 7.5 for 1 h at the boil; in the case of the less reactive MCTs, 1 h at 140°C was required to achieve adequate fixation values.

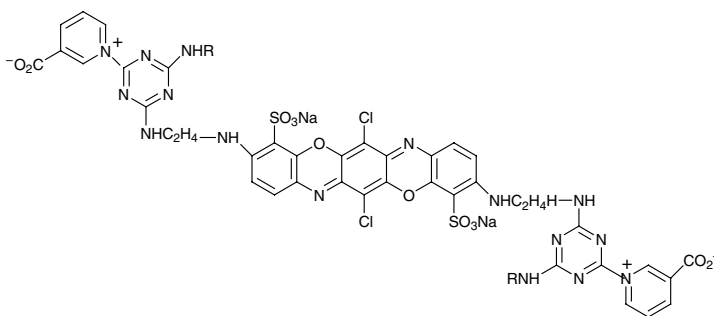




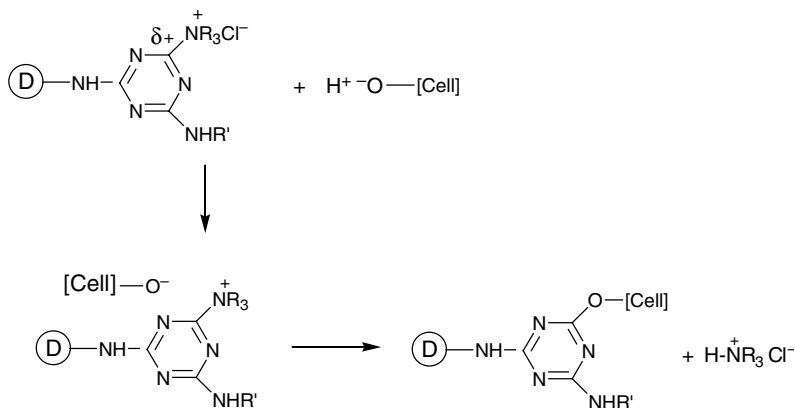
9.24 Synthesis of bis-MCT/DSBES dyes.



9.25 Preparation of a hetero-poly functional dye containing a disulphide-ethylsulphone cross-link and two quaternised triazine groups.



9.26 Procion Blue HE-G (C.I. Reactive Blue 187).



9.27 Possible ionic interactions prior to covalent bonding of quaternary-amino-*s*-triazine dye.

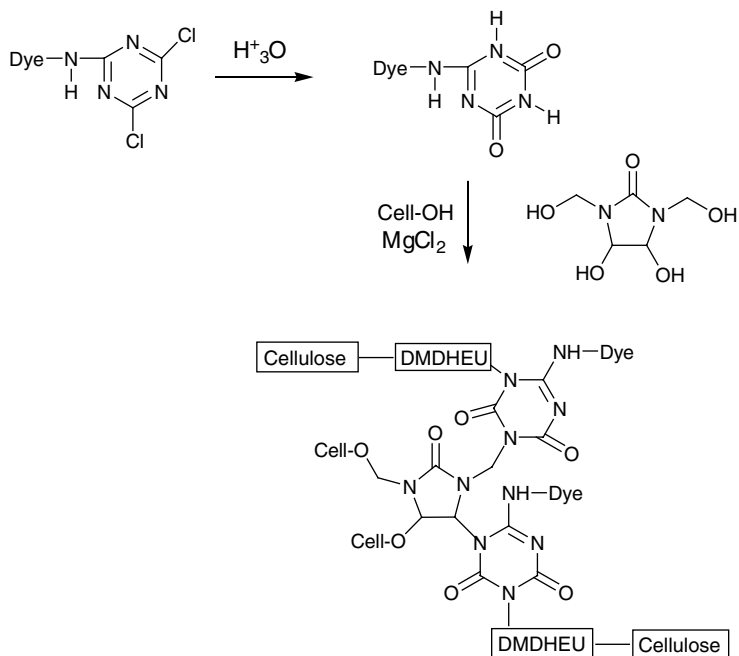
### 9.3.8 Acid fixing reactive dyes for cellulosic fibres

In order to improve the efficiency of cotton/polyester blend colouration, with mixtures of reactive and disperse dyes, mildly acidic fixation conditions would be desirable as many disperse dyes are alkali sensitive.

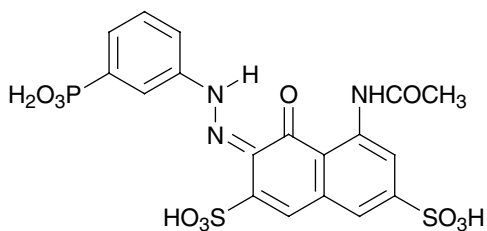
Early attempts to produce an acid-fixable system resulted in *N*-methylol-amino-*s*-triazine dyes from American Cyanamide (Calcobond dyes)<sup>39</sup> but these were subsequently withdrawn from the market. The above dyes were fixed in the presence of a Lewis acid catalyst such as magnesium chloride by a pad-dry-bake procedure.

The ICI Procion Resin process<sup>3</sup> is reminiscent of the above. In this case DCT dyes were mixed with a cotton durable-press cross-linking agent such as *N,N'*-dimethylol-dihydroxy-ethylene urea (DMDHEU) and magnesium chloride; the mix was padded on to cotton fabric, dried and cured at 170–180°C for 30 s; excellent fixation values were obtained. The procedure still finds practical use in the printing of cotton/polyester sheeting materials. The main problem on 100% cotton fabrics is loss of strength due to the acidic conditions employed. The mechanism for dye–fibre covalent bonding is presumably as shown in Fig. 9.28.<sup>40</sup>

Much effort has been directed at the covalent fixation of phosphonic acid containing dyes to cellulosic fibre substrates using a high temperature dry fixation procedure (thermofix) under mildly acidic conditions. In 1977 ICI introduced acid-fixable phosphonic acid dyes for the pad- or print-thermofix colouration of cellulosic fibres.<sup>41</sup> The research which formed the basis of this system was actually carried out at Stamford Research Institute and Burlington Industries<sup>42,43</sup> and resulted in a range of dyes derived from the



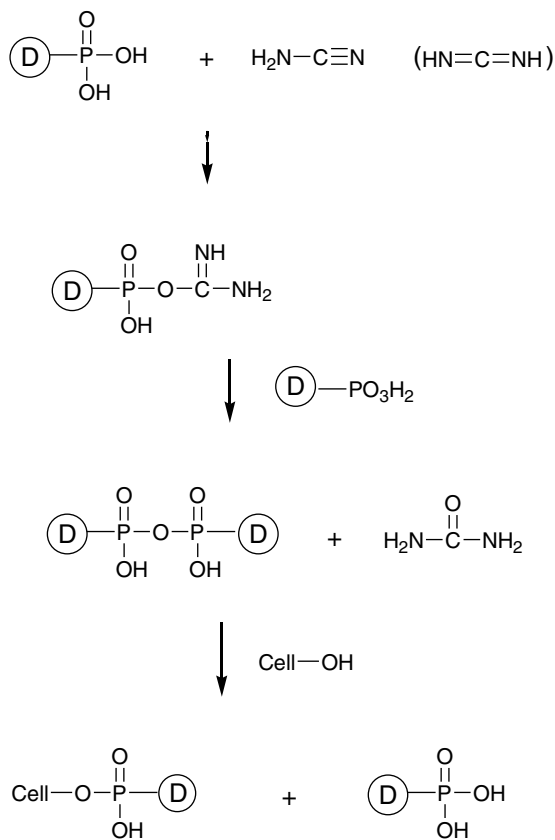
9.28 Cross-linking hydrolysed triazine dyes to cotton cellulose using DMDHEU.<sup>40</sup>



9.29 Procion Red T2B.

intermediate, *m*-aminobenzene-phosphonic acid, supplied by Stauffer. The range was sold as Procion T dyes and, in admixture with alkali dischargeable disperse dyes, as Procilene PC dyes for colouration of cotton/polyester blends. The structure of Procion Red T2B prepared from simple diazotisation of *m*-amino-benzene phosphonic acid and coupling this diazo salt to N-acetyl H-acid is shown in Fig. 9.29.

Despite the fact that phosphonate dyes could not hydrolyse during the application procedure to form the phosphonate ester bond with cellulose, only modest fixation efficiencies were recorded. It was important to include



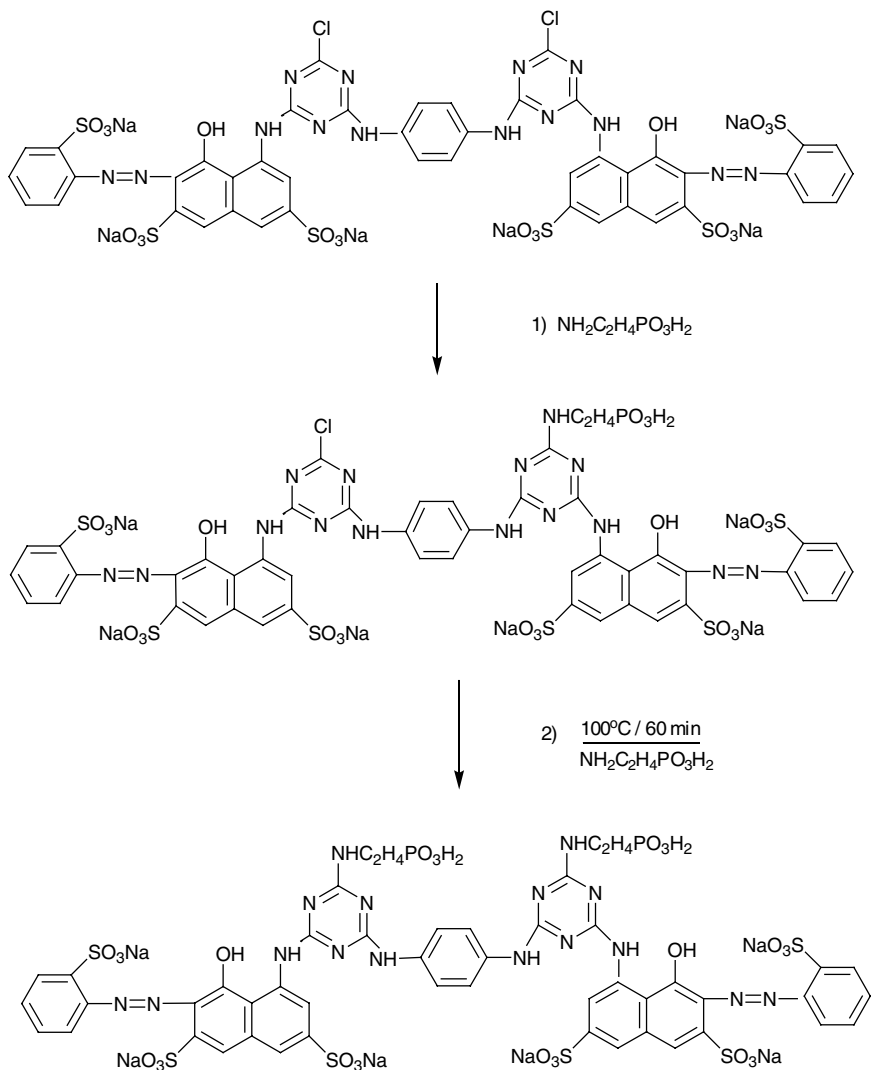
Where  $\textcircled{\text{D}}$  = sulphonated chromophore

### 9.30 Fixation of phosphonate dyes on cotton cellulose.

a dehydrating catalyst such as cyanamide or preferably dicyandiamide with the dye in order to promote the above esterification reaction. The above catalysts can form carbodiimide tautomers which are the dehydrating agents. Figure 9.30 shows the proposed reactions.

Aliphatic poly-phosphonate dyes have also been studied;<sup>44,45</sup> they were prepared by the simple expedient of condensing aminoethyl-phosphonic acid with existing bis-MCT reactive dyes according to Fig. 9.31.

In the above study, cotton fabric was padded with a pad liquor containing 120 g/L cyanamide, 10 g/L ammonium dihydrogen phosphate and 20 g/L pure phosphonate dye (it is important to prepare the dye as the



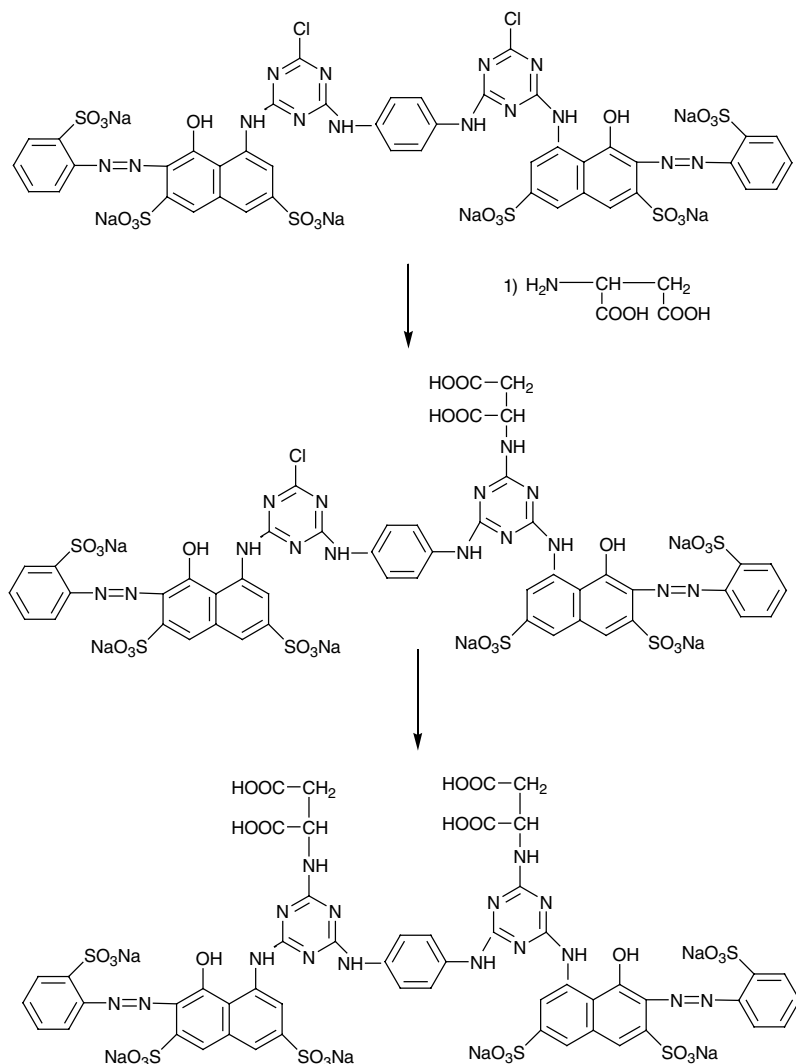
9.31 The reaction of C.I. Reactive Red 120 with aminoethyl-phosphonic acid.

ammonium salt); after drying and thermofixing at  $200^\circ\text{C}$  for 90 s the alkyl-phosphonate dyes gave 95% fixation whereas the mono-functional Procion T aryl-phosphonate dye gave only 46% fixation. Thus the fixation values of the alkyl-phosphonate dyes in thermofixation processes are outstanding; this result was for 2% o.m.f. pure dye which corresponds to a 3–4% shade of commercial dyes since the latter contain salt, buffers and de-dusting agents.

The dye–fibre phosphonic acid ester bond is remarkably resistant to treatments in acidic or alkaline media.<sup>46</sup>

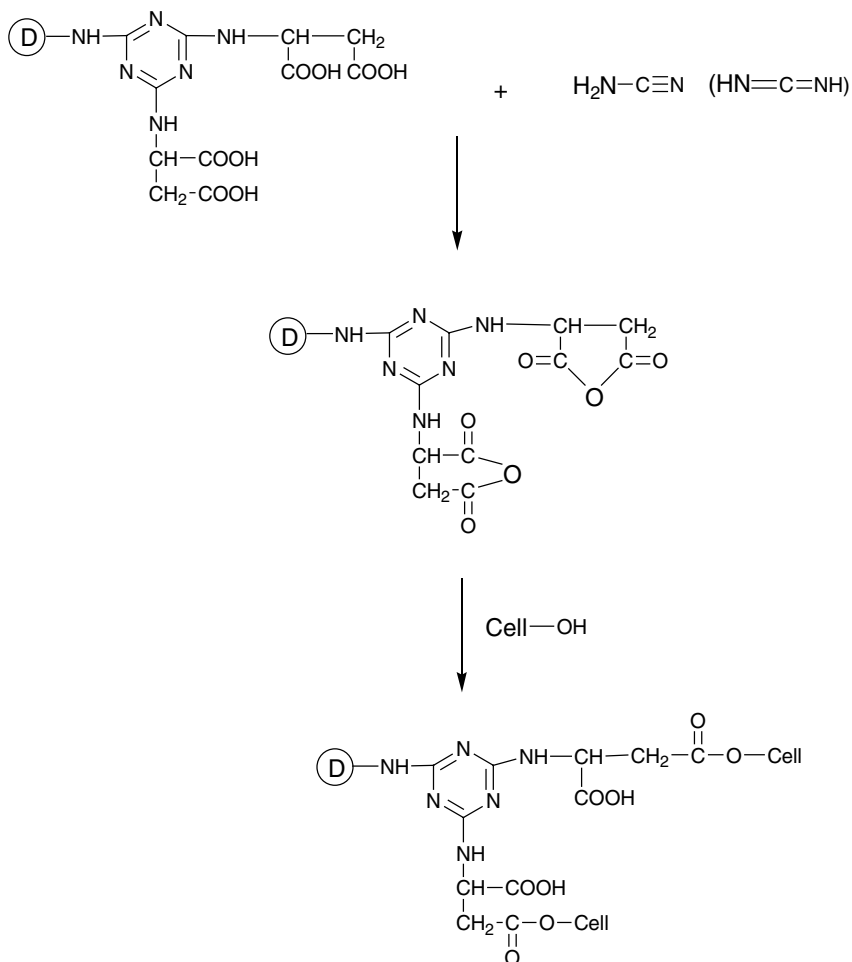
In a similar vein polycarboxylic acid containing dyes have been synthesised as their ammonium salts and applied to cotton by thermofixation procedures<sup>47</sup> in the presence of cyanamide as a catalyst. In this case aspartic acid was used to make 2,4-diaspartyl-*s*-triazine dyes according to Fig. 9.32.

The fixation values achieved when the above dye was applied to cotton by a pad-batch-thermofix (200°C, 90 s) procedure, from a pad liquor containing



9.32 The synthesis of a bis-aspartyl-*s*-triazine dye.

10 g/L pure carboxylate dye, 150 g/L of cyanamide and 10 g/L ammonium dihydrogen phosphate, were of the order of 75%. These results indicate that the system is not as effective as the phosphonate system perhaps due to the instability of the carboxylate ester dye-fibre bond under the alkaline (pH 10.5) boiling soaping-off conditions used. The fixation mechanism is shown in Fig. 9.33.



Where  $\text{D}$  is a sulphonated chromophore

9.33 Fixation mechanism for the reaction of a polycarboxylate dye with cellulose.

## 9.4 The application of reactive dyes to cellulosic fibres

### 9.4.1 Long-liquor or 'exhaustion' dyeing

A major use of reactive dyes is in long-liquor dyeing processes (exhaustion dyeing) and for these processes to operate efficiently three factors apply:

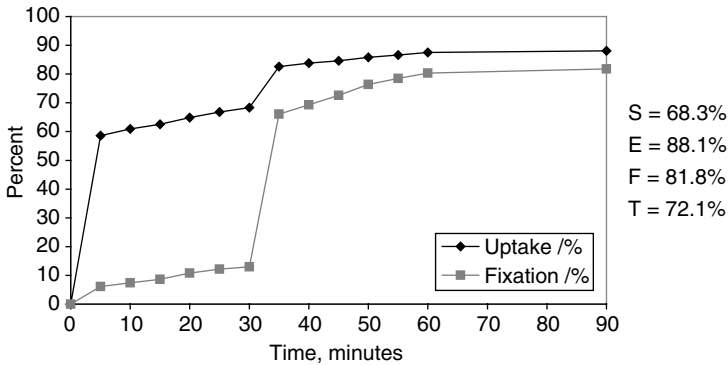
1. Dye substantivity must be as high as possible during the so-called neutral exhaustion phase (typically 30 min at the required dyeing temperature) – dye uptake by the fibre under these conditions involves minimal covalent bonding and most of the sorbed dye can usually be removed by cold water rinsing (with the exception of quaternised triazinyl dyes discussed later); the amount of dye sorbed at this stage may be expressed as %S (*substantivity factor*). The substantivity of the dye for the fibre during this phase of dyeing is almost wholly related to the salt concentration in the dyebath – with most reactive dyes, concentrations of sodium sulphate of 80 g/L are normal.
2. Following the above substantivity phase, an addition of alkali (usually sodium carbonate) is made and dyeing continued for a further 30 min to bring about covalent bonding of the dye with the fibre – dyebath exhaustion at this stage is referred to as %E (*exhaustion factor*).
3. At the end of dyeing, repeated rinsing in cold water and then in boiling water, until no more colour is removed, is carried out to remove all non-covalently bound dye. The amount of dye desorbed in these processes can be measured spectrophotometrically and hence the total efficiency of dye–fibre covalent bonding can be calculated as %T (*total fixation factor*). In some cases it may be useful to know the degree of fixation of the sorbed dye and this is referred to as %F; this factor is related to E and T by the simple relationship:

$$\%T = \%F \times \%E/100 \quad [9.1]$$

Exhaustion/fixation plots are very useful to study reactive dye compatibility in long-liquor dyeing.<sup>48</sup> Typical exhaustion/fixation curves for a sulphatoethylsulphonyl dye, C.I. Reactive Blue 19 (Remazol Brilliant Blue R), are reproduced<sup>49</sup> in Fig. 9.34 (the dyeing process used to obtain these results involved setting the dyebath at pH 7.0 at a 10:1 liquor ratio with 2% o.m.f. dye, 80 g/L sodium sulphate and running with cotton fabric for 30 min; 20 g/L tri-sodium phosphate was then added and the fixation step continued for 1 h).

Figure 9.34 shows that there is rapid uptake of this dye molecule in the 'salt-only' phase of dyeing and extremely rapid covalent fixation of the sorbed dye on addition of alkali. These kinetics indicate a potential for unlevel dyeing;





9.34 S, E, F and T profiles for a typical long-liquor reactive dyeing process.

Table 9.1 The fixation yield of various reactive red dyes

Dye	3% o.m.f.	6% o.m.f.
MCT/VS	76	68
MFT	64	56
MFT/VS	61	50
DFMCP	74	67
VS	68	58
MCT/MCT	57	49

MFT = monofluoro-*s*-triazine; VS = vinylsulphone;  
 DFMCP = difluoro-monochloro-pyrimidine  
 Source: Adapted from Douthwaite *et al.*<sup>50</sup>

therefore machines, such as jets, should be selected which give good mechanical interchange between the dye liquor and the goods being dyed. A further important feature, emerging from this study, is the T value of 72%; this value indicates that 28% of the dye originally applied is lost to the dye-house effluent; if deeper shades than the 2% applied in this case are used, the dye discharge problem increases greatly; Table 9.1 reinforces this observation.

### 9.4.2 Pad-batch, pad-steam and pad-bake piece dyeing processes

Padding processes now account for about 25% of cotton fabric dyeing procedures; this drop in popularity is because the industry has to respond to a high fashion market which increasingly demands short runs to a particular shade. Moreover it is costly to put together a padding system involving application of an excess of pad liquor which contains relatively high concentrations of

dye, some 20 L of which is simply washed to drain at the end of padding. In terms of energy saving pad-batch (24 h) is an important procedure, batching being carried out at 30°C in a constant temperature environment.

### 9.4.3 Printing processes

Rotary screen printing makes up the most important part of the market and there are many useful reviews of this area.<sup>51</sup> When printing cotton fabrics, reactive dyes of the highest possible solubility are required and their print paste stability is of paramount importance – alkaline (sodium carbonate) print pastes containing MCT or sulphatoethylsulphone dyes are preferred since they can be stored overnight without significant hydrolysis.

It is of interest to describe recent advances in the field of ink-jet printing of textiles. The advent of practically useful ink-jet printing systems has brought about an exciting technological revolution in such diverse fields as paper printing, electronic device printing, textile printing, micro-fabrication and even printing living tissue scaffolds.

#### *Ink-jet printing of textile substrates with reactive dye-based inks*

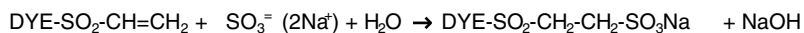
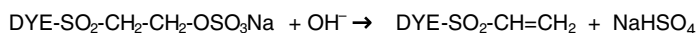
Currently commercial ink-jet textile printing operations require the pre-treatment of cellulosic fabrics with pad liquors containing a thickener and alkali (such as sodium carbonate or sodium bicarbonate). Broadbent and Lewis<sup>52</sup> found that this procedure can also use neutral fixation ‘activators’ such as sodium acetate, sodium formate, sodium trichloroacetate, sodium cyanate or sodium borate, all typically used at a concentration of 100 g/L. The results indicated that fabrics pre-treated, even at pH 6.5, by padding and drying such an ‘activator’ resulted in subsequent ink-jet prints that exhibited much higher levels of reactive dye fixation than corresponding prints produced on alkali pre-treated fabrics. The reactive dyes employed in the inks were selected from Remazol (sulphatoethylsulphone), Cibacron F (MFT), Cibacron C (MFT, vinylsulphone), Sumifix Supra (monochlorotriazine, sulphatoethylsulphone), Procion (monochlorotriazine), Drimarene K (difluoro-monochloro-pyrimidine) and Sumifix HF (modified vinylsulphone).

#### *Resist printing cotton with inks containing sodium sulphite*

Discharge printing provides a method of producing either a white or coloured image on a solid ground fabric; unfortunately the print shade range from this process is limited. An alternative approach to discharge printing is resist printing. In resist printing, the resist agent prevents fixation of the background colour by chemical means (resist agent inhibits dye fixation) or physical means (resist agent inhibits dye absorption), in both cases giving a white print against a solid colour background. A coloured print may be

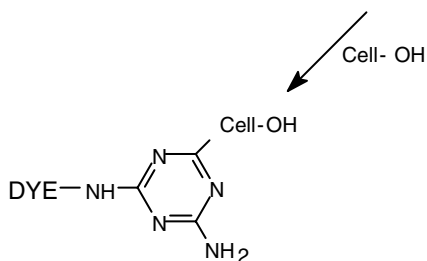
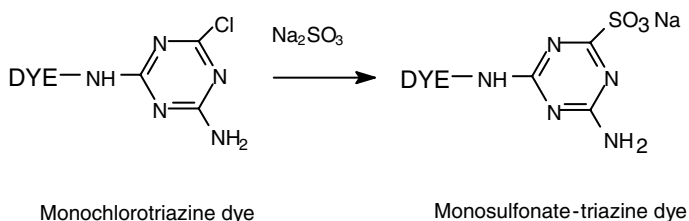
achieved by incorporating a suitable dye or pigment in the resist ink. In all cases it is *extremely important* that the ground-shade reactive dye(s) do not fix during the drying process prior to the printing process, otherwise white images cannot be produced following printing with the resist agent, then steam development and washing-off. A suitable process includes the following steps: pad the fabric with a pad liquor containing a sulphatoethylsulphone reactive dye (Remazol) and the metal salt of an organic acid (sodium formate to pH 6.5), dry at 70–80°C, overprint with a print paste containing either the sodium sulphite resist agent, or for illuminated prints sodium sulphite plus a monochloro-*s*-triazine reactive dye (Procion P/PX); fixation is achieved by steaming at 102°C for 8–10 min, finally soap-off to yield either a white and/or a coloured print on a coloured background.

The reactions occurring during the process are represented in Figs. 9.35 and 9.36.



Inactive sulfonate dye

9.35 Reaction of sulphatoethylsulphone dye with sulphite as the resist agent.



9.36 Reaction of monochlorotriazine dye with resist agent and cellulose.

Background fabrics for use in the ink-jet sulphite resist process could be prepared by padding and drying cotton fabric with a dye liquor containing Remazol dyes (either in the sulphatoethylsulphone or the vinylsulphone form), an activator (sodium formate or sodium acetate) and a thickening agent so as to achieve a wet pick-up of 100%; to inhibit possible background dye reduction by liberated  $\text{SO}_2$  in subsequent steaming, an anti-reductant, such as Ludigol (BASF), should be incorporated in the ground pad liquor. After padding, the fabrics were dried at  $50^\circ\text{C}$  for 3 min to yield coloured ground fabrics that could be used for subsequent resist printing operations. When using sodium formate as an activator, high levels of dye fixation were achieved for pad liquors possessing the Remazol dye in its pre-activated vinylsulfone form, whilst pad liquors containing sodium acetate gave equivalent results even when the Remazol dye was still in its sulphatoethylsulphone form. Weakly acidic pad liquors (pH 6.5) enabled the production of ground-shade fabrics having 4–5 days' stability (i.e. no dye–fibre bonding or dye hydrolysis), whereas ground fabrics prepared using alkaline pad liquors require immediate printing to prevent unwanted ground dye fixation occurring. White image areas can be achieved by printing these prepared grounds with resist inks formulated from sodium sulphite. The addition of a tertiary amine, such as DABCO, to the resist ink formulation resulted in improved ground-shade dye deactivation (ground shade produced using sodium formate) and so lower levels of sodium sulphite could be used. However, inks containing reduced sodium sulphite concentrations were not successful in fully resisting ground shades produced using sodium acetate, such ground fabrics still requiring the higher sodium sulphite concentrations to achieve total dye inactivation.

Illuminated resist inks contained both a resist agent (sodium sulphite) and a suitable sulphite-stable monohalo-*s*-triazine reactive dye. On ground fabrics containing sodium formate, it was observed that illuminating inks containing MFT dyes (Cibacron F) provided greater colour yields than corresponding inks containing monochloro-*s*-triazine dyes (Procion P/PX or Sumifix Supra).

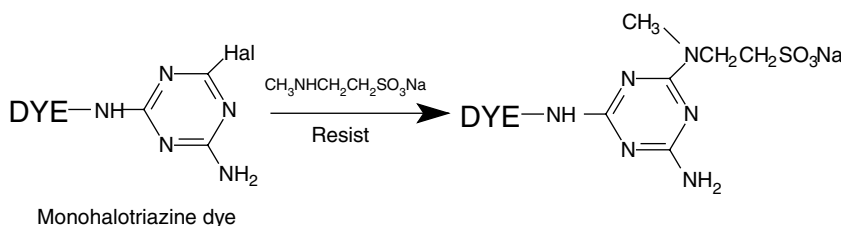
#### *Resist printing with secondary amines*

In terms of the dye class selection this system covers the opposite situation to the above sulphite process; in this case monohalo-*s*-triazine reactive dyes are padded on cotton fabrics and then ink-jet printed with a suitable secondary amine based ink formulation to produce a white image on a solid ground colour after appropriate fixation and soap-off procedures have been undertaken. A coloured image can be achieved by over-printing the resist printed areas with a coloured ink formulation containing either a vinylsulphone or a sulphatoethylsulphone reactive dye; such dyes are capable of forming a new reactive dye via reaction with a secondary amine and so are

not deactivated towards subsequent covalent reaction with the cotton substrate. The processes involved may be summarised by the following steps:

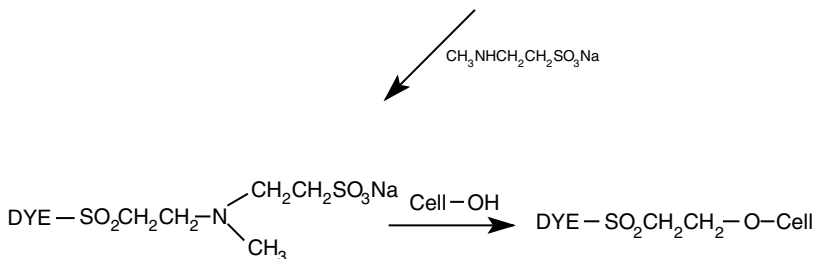
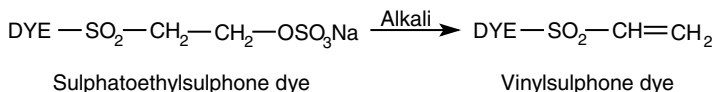
1. pad the fabric with a pad liquor containing a monohalotriazine reactive dye and the metal salt of an organic acid,
2. dry at 70–80°C,
3. overprint with an ink containing N-methyltaurine and, if colour resist prints are required, a sulphatoethylsulphone reactive dye,
4. steam at 102°C for 8–10 min,
5. soap-off to give either white only or coloured/white prints on a coloured background.

The reactions occurring during the process are represented in Figs. 9.37 and 9.38.



No dye-fibre reaction possible

9.37 Reaction of monohalo-s-triazine dye with N-methyltaurine.



9.38 Reaction of sulphatoethylsulphone dye with N-methyltaurine.

The ground shade for use in the secondary amine resist process may be produced by padding the cotton fabric with liquors containing an MFT dye (Cibacron F (Ciba)), a thickening agent, an anti-reductant (Ludigol (BASF)) and a dye activator such as sodium formate. In particular, sepia ground shades were prepared using the following pad liquor: 8 g/L Cibacron Red FN-R, 5 g/L Cibacron Blue FN-R, 12 g/L Cibacron Yellow F-3R, 8 g/L Cellcosan 2000, 20 g/L Ludigol, 50 g/L sodium formate (adjust to pH 5.0 with formic acid).

The fabrics were padded and dried at 50°C for 3 min on a Mathis laboratory drier – this low drying temperature ensured that no fixation of the reactive dyes occurred at this stage.

A dye activator, such as sodium formate, is added to promote the fixation of the ground dye under the mildly acidic conditions employed. The activator also promotes the fixation of the illuminating dye when coloured images are being printed on resisted ground fabrics. Ground fabrics prepared by the above processes could be stored at room temperature for 4–5 days without any unwanted ground dye–fibre fixation occurring. After such storage times, the prepared ground fabrics could still be printed with secondary amine based resist inks and processed to produce white images on a coloured ground.

White (secondary amine resist process) ink formulations may be prepared using 10–100 g/L N-methyltaurine (secondary amine), 150 g/L ethylene glycol, 20 g/L 2-pyrrolidinone and 25 g/L propan-2-ol (adjust to pH 5.0 via the addition of formic acid and make up to 1 L with distilled water); the process of ground dye inactivation by N-methyltaurine is indicated in Fig. 9.37. Such inks enabled white images to be produced on coloured ground shades. Alternatively, coloured images can be prepared by either including an illuminating dye, such as a Remazol (Dystar), Sumifix Supra (Sumitomo), Sumifix HF or Cibacron C dye, in the resist ink formulation, or by over-printing image areas previously printed with the white resist ink formulation.

Illuminated resist ink formulations capable of producing multi-coloured images on a coloured ground were formulated in accordance with the following recipe: 50 g/L N-methyltaurine, 100 g/L Remazol dye, 200 g/L N-methylmorpholine-N-oxide, 20 g/L 2-pyrrolidinone and 25 g/L propan-2-ol (adjust to pH 5.0 via the addition of acetic acid and make up to 1 L with distilled water).

The vinylsulphone-containing dyes used to prepare the illuminating inks included the following: Sumifix Supra Red 3BF, Sumifix Supra Yellow 3RF, Sumifix Supra Turquoise Blue BGF, Sumifix Supra Blue BRF, Remazol Red BS, Remazol Turquoise Blue G, Remazol Golden Yellow RNL, Remazol Brilliant Blue R, Remazol Brilliant Red F-3B, Sumifix HF Yellow 3R, Sumifix HF Red 2B, Sumifix HF Blue 2R, Cibacron Red C-R, Cibacron Blue C-R and Cibacron Yellow C-2R.

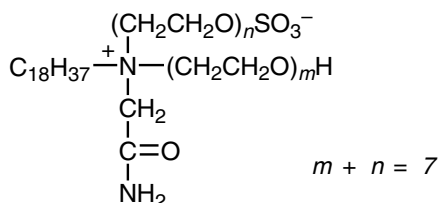
## 9.5 The application of reactive dyes to natural and synthetic polyamide fibres

### 9.5.1 Reactive dyes for wool

As discussed previously wool featured highly in early developments of reactive dyes; in particular the  $\omega$ -chloroacetyl amino reactive group appeared as early as 1938 in the IG dye Supramino Orange R, and Ciba put together a small range of bright wool dyes containing this grouping in 1954 (Cibalan Brilliant); in 1952 Hoechst marketed Remalan and Remalan Fast, 2:1 pre-metallised reactive dyes for wool<sup>11,12</sup> which contained pendant sulphatoethylsulphone residues capable of elimination to vinylsulphone reactive groups when applied from boiling dyebaths above pH 5.0. Hoechst even sold chrome dyes with the sulphatoethylsulphone residue being incorporated in the dye molecule, these being Metachrome Orange H-3R, Metachrome Gey RL, Salicinchrome Orange H-3R and Salicinchrome Grey RL.

The above early reactive dyes for wool gave considerable problems of unlevel dyeing, especially in piece dyeing and yarn hank dyeing, and thus their usage was mainly in loose stock and top dyeing. A major advance in level dyeing reactive dyes on wool occurred in 1966 with the launch of the Lanasol dyes (Ciba-Geigy); these dyes were based on the  $\alpha$ -bromoacrylamido group<sup>24, 25</sup> and were sold with the very important level dyeing auxiliary, Albeval B. Albeval B is an amphoteric product which probably has the general structure illustrated in Fig. 9.39.<sup>53</sup>

Many of the unlevelness problems associated with reactive dyeing of wool were alleviated by dyeing with this novel product. By happy coincidence the launch of the Lanasol dyes coincided with the marketing of truly machine washable wool, produced by the continuous chlorine–Hercosett treatment of wool tops, a process developed by scientists at CSIRO and IWS.<sup>54</sup> Other companies subsequently entered the wool reactive dye market, Bayer and Sandoz launching difluoro-monochloro-pyrimidine dyes (Verofix/Drimalan F)<sup>55</sup> and Hoechst launching a reassembled range of blocked vinylsulphone dyes (Hostalan).<sup>56,57</sup> Dyeings produced on the chlorine–Hercosett-treated substrate with acid dyes, acid milling dyes and pre-metallised dyes did not



9.39 Amphoteric levelling agent for reactive dyeing of wool.

show adequate wash-fastness properties but dyeings produced with reactive dyes gave outstanding washing performance.<sup>58</sup>

#### *Modern usage of reactive dye systems in wool dyeing*

In the light of increasing environmental concerns with heavy metals it is now usual to use reactive dyes to match deep shades of black and navy blue in order to offer the dyer a real alternative to chrome dyes. In this context dye manufacturers have increased their efforts to offer wool dyers ranges of reactive dyes which are attractively priced; examples include Lanazol CE dyes from Ciba, Realan dyes from DyStar and Drimalan dyes from Clariant.

Black and navy blue shades are often based on the popular and widely available dye, the bifunctional sulphatoethylsulphone C.I. Reactive Black 5, which slowly activates, *in situ*, to its fibre-reactive vinylsulphone form on boiling at pH 5.5.

In the light of environmental concerns about absorbable organo halogen (AOX) in effluents, Müller<sup>59</sup> has studied AOX residues from various reactive dye systems; in this context there are advantages in selecting reactive dyes containing only sulphatoethylsulphone residues as the reactive group.

#### *Developments in reactive dyes for wool and their role as anti-setting agents*

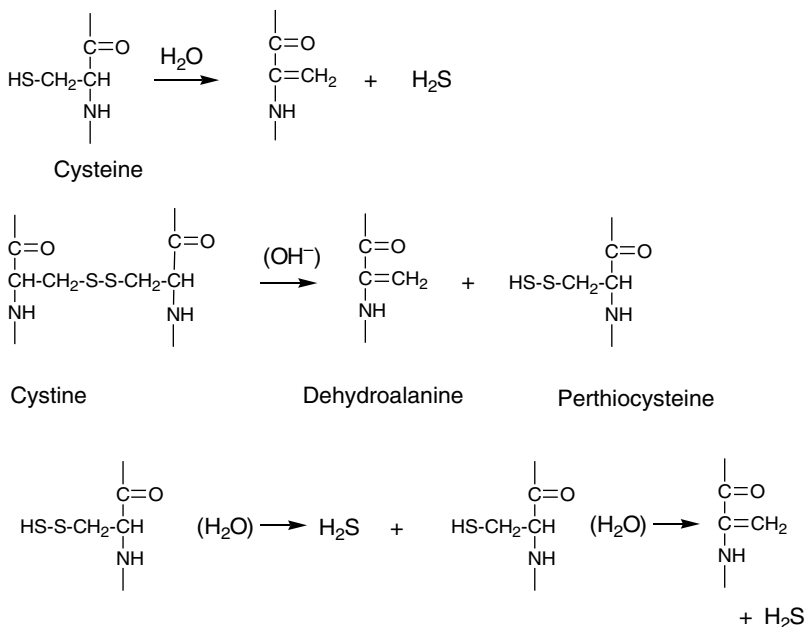
The chemistry of reactive dyes for wool has been fully reviewed.<sup>60,61</sup> Of particular interest is the ability of certain reactive dyes to interfere with setting. Permanent setting is a contributory factor to loss in wool fibre strength during dyeing, is the main cause of increased hygral expansion of wool fabrics following piece dyeing, is the reason for surface marks such as 'crow's-feet' in piece dyeing and is the source of reduced bulk or yarn leanness following package dyeing.<sup>62-64</sup> Apart from the above wholly negative effects, permanent setting can sometimes be seen as beneficial: such instances include the setting of wool yarn in hank form when using hank dyeing machines – this gives extra bulk and resilience to yarns and explains why this dyeing route remains popular for the production of dyed wool yarns for carpets. It is necessary to summarise the various chemistries involved in the production of permanent set in wool dyeing.

Wool is a heterogeneous material made up to keratin proteins, a small amount of non-keratinous proteins and even smaller amounts of lipid and fatty acid materials. It is the keratinous or cystine disulphide cross-linked proteins which are responsible for most of wool's physical properties and the reactivity of the cystine disulphide residue is of paramount importance. The cystine content of wool varies but an appropriate average value is 450  $\mu\text{mol/g}$  and for its reduced form, cysteine, 30  $\mu\text{mol/g}$ . Cystine and its reduced form cysteine are particularly sensitive to elimination reactions in water, the extent and nature of which depend especially on the parameters pH, temperature and time.<sup>65-67</sup>

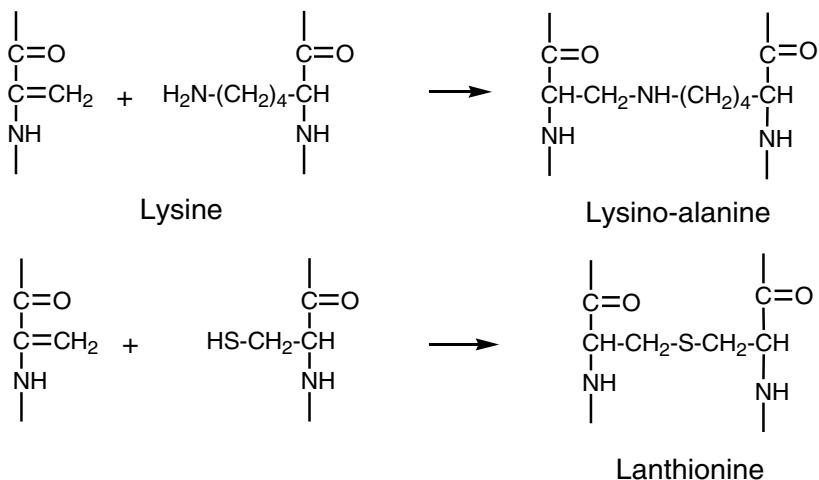


These sulphur containing amino acid residues can readily undergo a *trans* 1,2- $\beta$ -elimination reaction, especially in aqueous environments, to form the dehydroalanine residue which contains an activated double bond capable of subsequent Michael addition with suitable nucleophiles. The above elimination reactions are activated by the electron withdrawing character of the adjacent amide carbonyl residue. In general the thiol form, cysteine, more readily undergoes  $\beta$ -elimination than the disulphide form, cystine (Fig. 9.40).

The hydrogen sulphide or hydrosulphide anion produced in the above reaction is capable of ready reaction with cystine disulphide residues to produce further cysteine thiol residues which will undergo rapid  $\beta$ -elimination to dehydroalanine and hydrogen sulphide in boiling dyebaths even at pH 3.0; this is clearly the start of a runaway degradation reaction. The reactive entity, dehydroalanine, will undergo Michael addition with amino nucleophiles present in histidine and lysine residues and with thiol nucleophiles present in cysteine; in this way, more stable cross-links such as histidino-alanine, lysino-alanine and lanthionine are formed.<sup>68,69</sup> The extent and exact composition of these new cross-linking amino acids varies greatly with pH and temperature of treatment, since the nucleophilicities of amino and thiol residues increase with pH and temperature increases. The chemistry of these cross-linking reactions is exemplified, for lysine and cysteine residues, in Fig. 9.41.



9.40 Elimination reactions of wool cysteine and wool cystine.



9.41 The formation of lysino-alanine and lanthionine cross-links.

The above cross-links will not undergo degradation or elimination reactions under conditions normally encountered in wool dyeing and are thus likely to be of great importance in explaining the phenomena of permanent setting during wool dyeing. Also of some importance in setting is the so-called thiol–disulphide interchange reaction.<sup>70,71</sup>

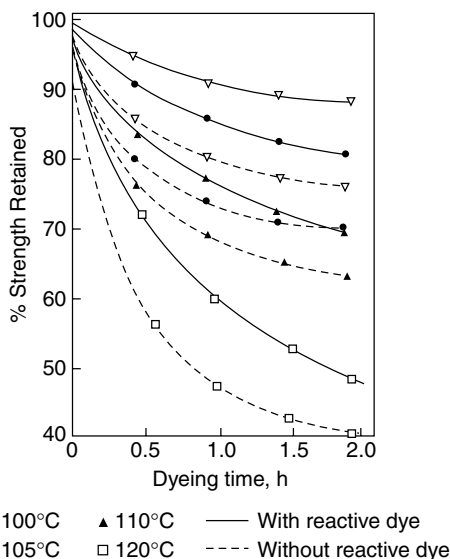
The above discussion indicates that inhibition of setting in wool dyeing can be achieved in two ways:

1. inclusion of oxidants in the dyebath
2. inclusion of fibre-substantive electrophiles in the dyebath.

Most of the published research in this area uses K pkes crease angle method for measuring set.<sup>72</sup> Typically including an anti-setting agent when dyeing wool at pH 5.0 for 1 h at the boil will reduce this measured set value from *ca.* 70% to *ca.* 30%.

Selected reactive dyes actively prevent damage in wool dyeing;<sup>73</sup> particularly effective are those dyes which contain activated carbon-carbon double bonds and which thus react with fibre nucleophiles via a Michael addition mechanism (these dyes include acrylamido dyes and vinylsulphone dyes). The magnitude of this effect increases with increasing amounts of reactive dye applied being optimum at *ca.* 3% dye o.m.f. The importance of this effect when dyeing wool fabric at pH 4.0 with the  $\alpha$ -bromoacrylamido reactive dye, Lanazol Red 6G – 4% o.m.f., is demonstrated in Fig. 9.42.

It is interesting to reflect why reactive dyes based on reactive halogenated heterocycles, which react with wool fibre nucleophiles by a nucleophilic substitution reaction, are less effective in controlling wool damage in dyeing than

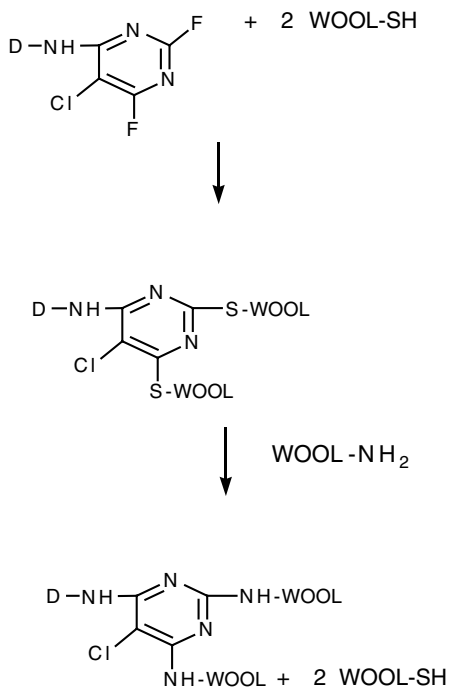


9.42 Effect of time, temperature and Lanazol reactive dye on fabric strength.<sup>73</sup>

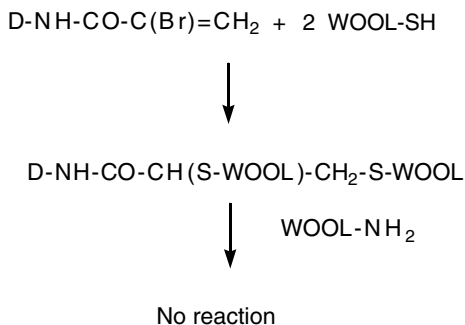
are the activated carbon-carbon double bond type of reactive dye. From the above discussions it is clear that successful control of damage and set go hand-in-hand and it is thus necessary to look carefully at the reactivity/stability of the reactive dye-cysteinyl residue covalent bond. Thioether derivatives of triazine or pyrimidine heterocycles will react further with amines to form bonds of greater stability; the leaving group in this reaction being the substituted thiol.<sup>74</sup> The thioether formed from reaction with an activated carbon-carbon double bond is, however, resistant to nucleophilic attack or  $\beta$ -elimination under the mildly acidic conditions pertaining in wool dyeing.<sup>75</sup>

When set was measured from wool fabric dyeings produced at pH 5.0 from the activated halogenated heterocycle type of reactive dye, Drimalan Red F-2G – Clariant (3% o.m.f.), a value of 74% was obtained; in contrast when the above dye was replaced with a reactive dye containing an activated carbon-carbon double bond, Lanazol Red 6G – CIBA (3% o.m.f.), a set value of 41% was obtained.<sup>76</sup> The reactions responsible for these differences are summarised in Fig. 9.43.

Cho *et al.*<sup>77</sup> also showed that the tri-functional reactive dye prepared, as shown in Fig. 9.44, gave excellent overall fixation efficiencies, greater than 95% for a 2% shade of pure dye, when applied to wool at pH 4.0 for 1 h at the boil; in comparison the best fixation values obtained from existing commercially available reactive wool dyes (e.g. Lanazol, Realan or Drimalan) are around 80%.

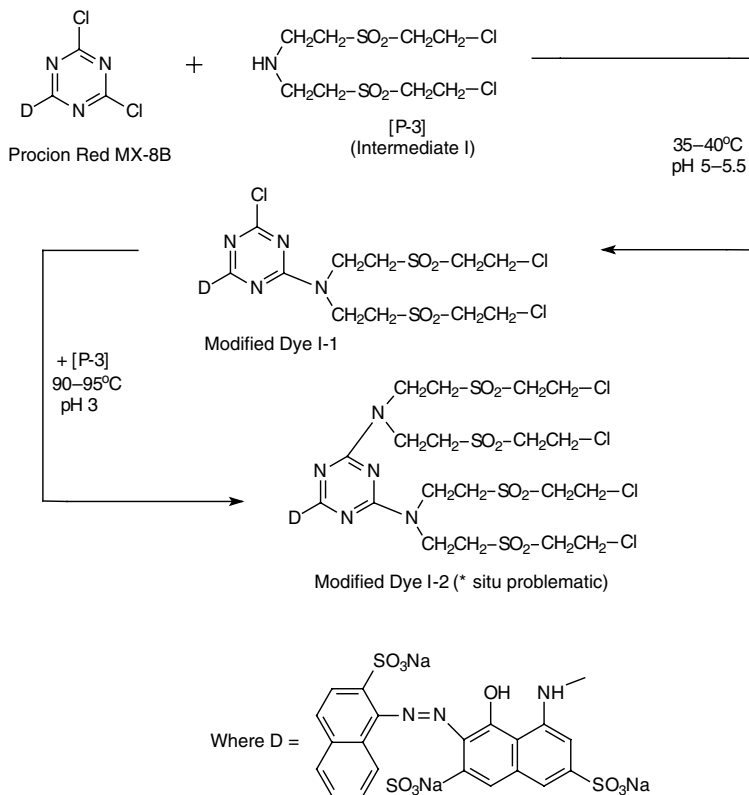


Activated carbon-carbon double bond dye:

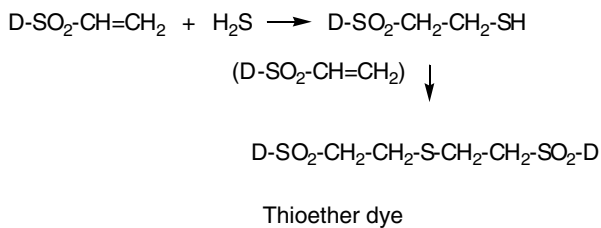


9.43 Cysteinyl reactions with active heterocyclic and double bond types of reactive dye.

The importance of hydrogen sulphide as a catalyst to promote setting/wool damage under dyeing conditions was proven by Lewis and Smith<sup>78</sup> who demonstrated the presence of a bis-(dye-sulphonylethyl)-thioether dye after dyeing with a model vinylsulphone dye. This dye arises from the reaction of the vinylsulphone with free hydrogen sulphide, according to the mechanism shown in Fig. 9.45.



9.44 Preparation of a tri-functional reactive dye suitable for wool dyeing.



9.45 Trapping of hydrogen sulphide by a vinylsulphone dye.

*Table 9.2* Fixation values for free vinylsulphone dyes on silk

Dye	Concn. (% o.m.f.)	E (%)	F (%)	T (%)
C.I. Reactive Blue 19	2	100	97	97
	3	100	96	96
	4	98	94	92
	5	96	92	88
C.I. Reactive Black 5	2	99	93	92
	3	98	93	91
	4	97	92	89
	5	96	90	86

### 9.5.2 Reactive dyes for silk

Compared with wool, silk has a much lower content of primary amino residues, 0.150 mol amine per kg versus 0.820 mol amine per kg. Hoechst recommended that silk should be dyed with sulphatoethylsulphone dyes (Remazol) at 60°C in the presence of Glauber's salt, adding 2 g/L soda ash to fix the dye after a few minutes.<sup>79</sup> Lewis and Shao<sup>80</sup> found that better results, in terms of levelness, colour yield and fixation, could be achieved by the following method: pre-activate the sulphatoethylsulphone (SES) dye to its vinylsulphone form by treatment in an aqueous solution at pH 8.0 for 5 min at the boil and then dye for 40 min at 80°C with this solution at pH 4.0–4.5 in the absence of salt.

Typical E, F, T values obtained for C.I. Reactive Blue 19 and C.I. Reactive Black 5 are summarised in Table 9.2.

### 9.5.3 Reactive dyes for nylon

Attempts to dye nylon fibres with reactive dyes have been frustrated by the paucity of nucleophilic sites available for reaction; typically nylon 6,6 from DuPont contains only 0.036 moles of free amine per kg of fibre which contrasts greatly with wool (0.820 mol amine per kg) and silk (0.150 mol amine per kg). This factor alone has meant that achieving build-up of sulphonated dyes even in moderate depths of shade is impossible, since every dye molecule covalently fixed means that, depending on the chromophoric component, one, two or even three strongly anionic sulphonate groups become fixed at the same time, resulting in a build-up of negative charge on the fibre which acts as a resist to further anionic dye uptake.

In the light of the above it is not surprising that the first range of reactive dyes for nylon was based on disperse dyes containing a pendant reactive group; these dyes were marketed as Procynyl dyes by ICI in 1959 and contained a variety of reactive groups, all but the yellow requiring alkali activation to form a more reactive residue.

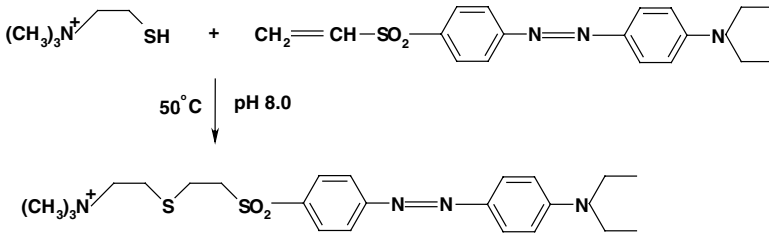
The dyes were all applied at the boil for 30 min under neutral conditions, the pH was then raised to 10.5 by the addition of sodium carbonate and boiling continued a further 30 min. The alkaline processing step achieved two objectives; firstly the amino end groups in nylon would not be significantly protonated giving maximum nucleophilicity, and secondly chlorohydrin groups in Procynyl Blue RS were converted to the highly reactive epoxide form or the chloroethylaminosulphonyl groups in Procynyl Scarlet GS, Procynyl Orange G and Procynyl Red GS were converted to the highly reactive aziridinylsulphone form. Scott and Vickerstaff<sup>81</sup> described the interesting chemistry behind these dyes and the application process, and demonstrated that in full shades of Blue RS or Scarlet GS more than the theoretical amount of dye, based on an amino end group content of 0.0426 mol per kg of fibre, could be covalently bonded to the substrate. In particular, results with Scarlet GS were very surprising; applying 20% dye (on mass of fibre) gave 0.1280 mol of dye per kg of fibre as covalently bonded dye. To explain this excess fixation given the paucity of amino groups, double addition of the dye at each amino residue is clearly possible as is reaction with ionised hydroxyl nucleophiles in the dye itself.<sup>82</sup>

The use of the vinylsulphone-type dye, C.I. Reactive Blue 19 for dyeing nylon has been studied in detail;<sup>83</sup> it was shown that this dye in the  $\beta$ -sulphatoethylsulphone form did not react efficiently with the available amino nucleophiles when applied at pH 5.0; if the dye was pre-converted to the vinylsulphone form before dyeing, then much better fixation efficiencies were observed.

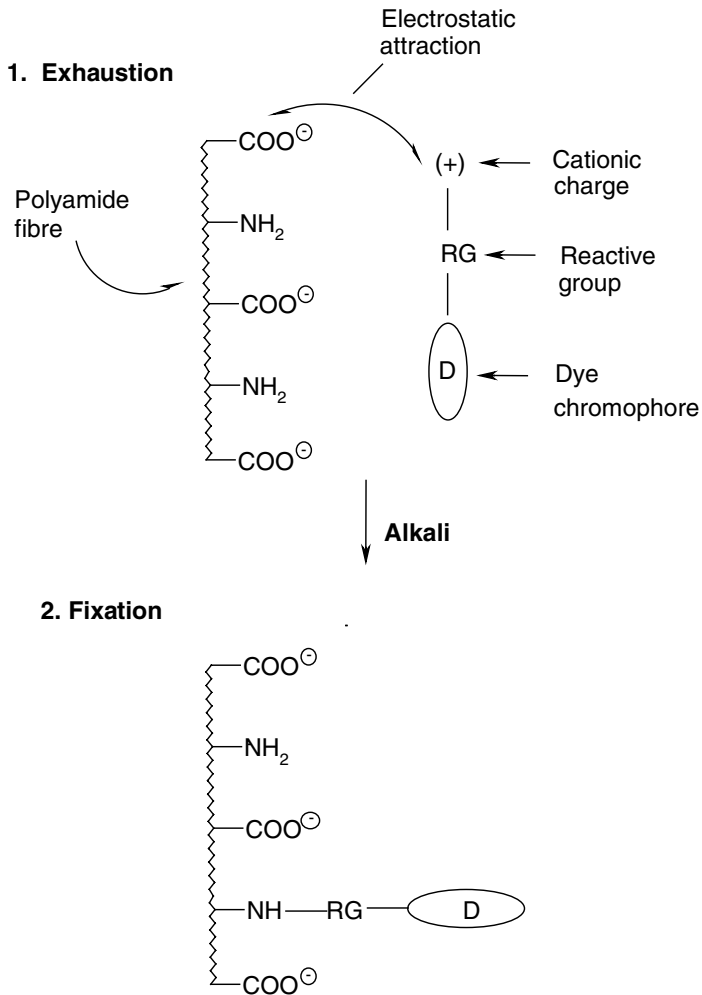
A cationic reactive dye of the general formula  $H_2C = HC-SO_2-D-Q^+$ , where D is an azo chromophore and Q is a quaternary ammonium residue, was prepared by Hinks *et al.*<sup>84</sup> and shown to dye nylon efficiently at pH 9.0. Substantivity of this cationic dye for nylon is high under alkaline conditions since the nylon is overall negatively charged and, in addition, the amino groups are more nucleophilic since they are likely to be deprotonated.

Sun and Lewis<sup>85,86</sup> published details of the synthesis of blocked vinylsulphone dyes using 2-thiol-choline – in these dyes the solubilising group was the trimethylammonium cation. When applied to nylon at pH 10.0 the dyes showed excellent substantivity and yet at the boil the thiol-choline residue was eliminated to form the vinylsulphone dye which reacted readily with the deprotonated amines in nylon. The preparation of this type of dye is shown in Fig. 9.46 whereas Figs. 9.47 and 9.48 describe the proposed absorption and reaction mechanism with nylon.

When a 2% dyeing (1 h at the boil) was carried out on nylon, from baths buffered at pH 3.0–10.0, with the pure cationic thio-choline dye exhaustion/fixation values were obtained as illustrated in Table 9.3. The total efficiency value of 93% with these cationic reactive dyes is impressive since anionic vinylsulphone dyes give maximum T value of 85% at 2% dye o.m.f.

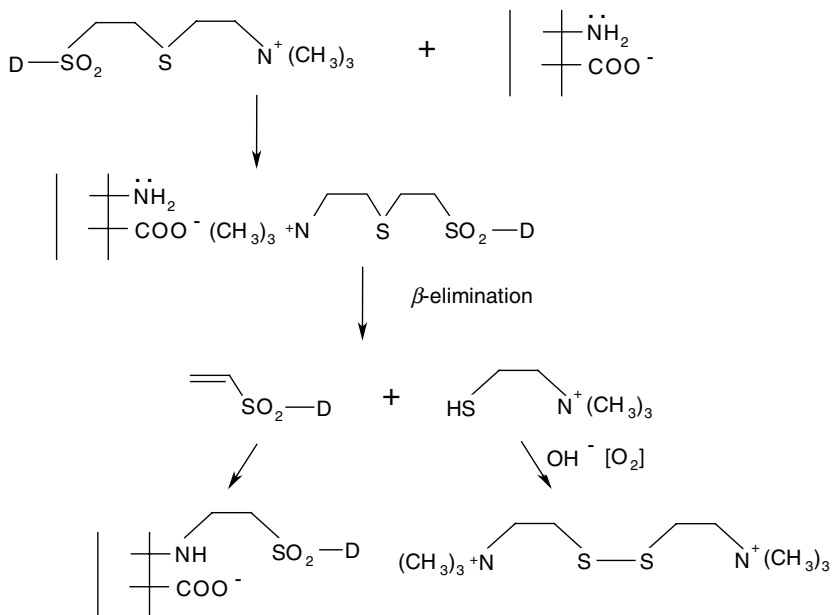


9.46 The reaction of thiol-choline with the VS disperse dyes to give a water-soluble cationic dye.



9.47 Proposed dyeing mechanism when dyeing cationic reactive dyes on polyamide fibres under alkaline conditions.





9.48 Absorption and reaction of choline-thioether-ethylsulphone dye with nylon under alkaline conditions.

Table 9.3 Exhaustion and fixation values for cationic reactive dyes on nylon (2% pure dye)

pH (dye bath)	E (%)	F (%)	T (%)
3	3.5	1.9	0.1
4	13.5	11.5	1.6
6	48.8	46.6	22.8
7	93.1	89.2	83.0
8	94.4	91.3	86.2
9	95.4	92.4	88.2
10	97.5	95.2	93.0

## 9.6 Miscellaneous methods to covalently bond dyes to fibres

### 9.6.1 Cellulose modification to enhance dye–fibre covalent bonding

The fixation of reactive dyes on substrates containing amino groups is much higher than on cellulosic substrates. Thus wool, which contains amino terminal groups on individual amino acid side-chains, can be dyed with reactive

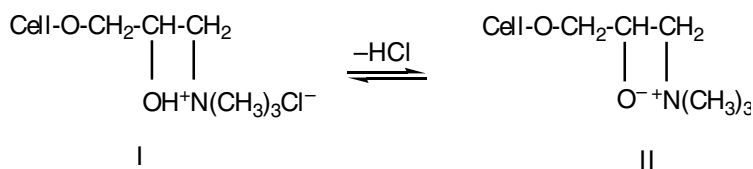
dyes from baths set at pH 5.0–7.0, to give very high fixation efficiencies. In some cases, total overall colour yields (fixation  $T$ ) of 95–100% are recorded, even in moderate depths of shades. These excellent results on wool are achieved without the need to add electrolyte. It is therefore not surprising that a large amount of work has been done to prepare modified cellulosic substrates containing amino residues in order to improve dyeability.

At one time, it was thought that a cheap and convenient way of modifying cotton to make it readily reactive dyeable was to pre-treat it, from a long-liquor, with a reactive cationic polymer under alkaline conditions.<sup>87</sup> Such treatments imparted a very high neutral substantivity for reactive dyes, in the absence of electrolyte, and gave dyeings of good wet-fastness. However, such approaches have not met with commercial success, as the treated fabric dyed to duller shades than those produced by the conventional salt/alkali process and a significant drop in light-fastness of 1–2 points was noted.<sup>88</sup>

Bright, light-fast dyeings could, however, be obtained by using a variety of methods to incorporate amino residues on cellulosic substrates and some of the most promising techniques will be discussed.

Rupin *et al.*<sup>89,90</sup>, Rippon<sup>91</sup> and Lewis and Lei<sup>92</sup> studied the dyeability of cellulose substrates modified with glycidyl-trimethyl-ammonium chloride (Glytac A from Protex) or its precursor 1-chloro-2-hydroxy-3-trimethyl-ammonium-propane chloride. This modification may be carried out by an alkaline pad-bake (200°C) or by an alkaline pad-batch procedure. Unfortunately, the product has insufficient substantivity to allow its application by long-liquor methods. The modified substrate may be considered to have the structure shown in Fig. 9.49, although the possibility of such treatments leading to the introduction of oligomeric polyether chains, bearing cationic functionality, has not been established.

The ease of neutral dyeing of this substrate with reactive dyes led Lewis and Lei<sup>92</sup> to speculate that the deprotonated form II predominates even when dyeing at pH 7.0. Thus, the anionic sulphonated reactive dye is initially absorbed on to the fibre by a powerful ionic attraction to the quaternary ammonium residue and fixes to the adjacent ionised (nucleophilic) hydroxyl group. Typical dyeing conditions that could be employed were



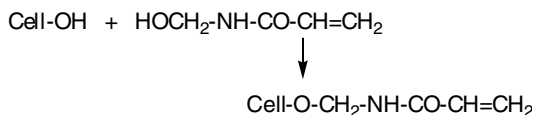
9.49 Different forms of cotton modified with Glytac A.

pH 7.0, with *no salt*, the bath being raised to the boil over 30 min and dyeing continued at the boil for a further 60 min. Dyeing, for example, with a 2% o.m.f. shade of C.I. Reactive Red 5 (DCT dye) gave exhaustion values of 85% and even more interestingly, 99% of the absorbed dye was apparently covalently fixed; thus soaping-off the dyeing gave rise to hardly any colour removal. Colour yields compared to the conventional salt/alkali method on untreated cotton were doubled.

Due to perceived health and safety problems in handling the epoxide form, recent efforts to modify cotton in this manner have concentrated on a pad-batch procedure; the 3-chloro-2-hydroxy-N, N,N-trimethyl propanaminium chloride (TAHC) is metered into the pad liquor along with sodium hydroxide solution to give final pad liquor containing 65 g/L TAHC and sodium hydroxide 50 g/L.<sup>40,93</sup> The high pH converts the above agent, during the batching procedure, to the corresponding epoxide which then fixes covalently to the fibre. The treated cotton can be dyed with selected reactive dyes in the absence of salt; dyebath exhaustion is 99–100%, even in full depths of shade, and fixation values also equal or approach 100%. Clark<sup>40</sup> showed that vinylsulphone-containing reactive dyes gave noticeably duller shades on the quaternary amine pre-treated cotton than did reactive dyes based on triazine or pyrimidine; this was attributed to the strong electron withdrawing character of the bonded sulphone group creating an anionic site which can ion-pair with the quaternary ammonium residue.

Lewis and Lei<sup>90</sup> also prepared a water-soluble cationic agent from the reaction of dimethylamine and epichlorohydrin and found that it would fix to cotton by an alkali catalysed pad-dry-bake procedure. The constitution of such products was not established; however, generation of an ionene-type cationic polyelectrolyte could be a possibility. In an analogous manner to the glycidyl-trimethylammoniumchloride (Glytac A) pre-treatment, the above agents gave a substrate which was readily neutral dyeable, at the boil, with reactive dyes, in the absence of electrolyte. Such dyeings exhibited wet- and light-fastness properties that mirrored the performance of the selected reactive dye applied to untreated cotton by the normal salt/alkali process.

An alternative method of introducing different aliphatic amino groups into cotton involved a pad-bake pre-treatment of the fabric with N-methylol acrylamide (NMA), which reacted covalently with cellulose by a Lewis acid catalysed baking reaction<sup>92</sup> (Fig. 9.50).



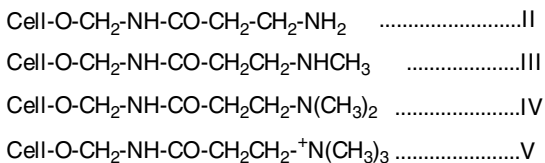
9.50 Reaction of NMA with cotton.

Reaction of the above substrate with appropriate amines gave a series of amino-substituted cellulosic substrates (Fig. 9.51).

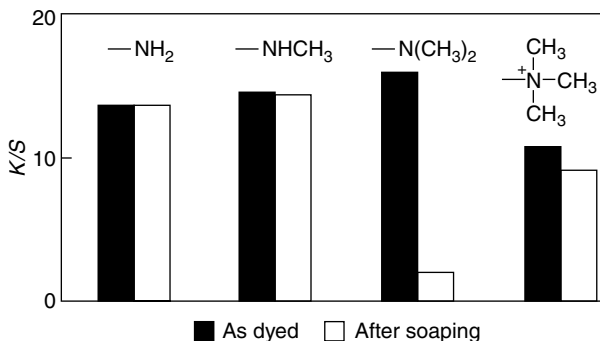
Substrates II–V inclusive were dyed at pH 5.0 in the absence of electrolyte, with 2% o.w.f. C.I. Reactive Red 5, raising the bath to the boil and boiling for 1 h. The results, in terms of colour yield (K/S) before and after soaping-off, are illustrated in Fig. 9.52. A study of this figure reveals that optimum exhaustion/fixation values are achieved on substrates II and III; substrate IV containing the tertiary amine gives surprisingly poor fixation results.

Undoubtedly the highly reactive DCT dye is likely to form a quaternary derivative with the tertiary amine residues in substrate IV and, failing reaction with a nearby fibre bonded nucleophile, this highly reactive species will rapidly hydrolyse. The work on substrate IV only involved highly reactive DCT dyes; with hindsight it is likely that more useful results could have been obtained on dyeing the substrates with MCT dyes, since in this case any quaternary triazine derivatives formed would be stable under acidic to neutral conditions.

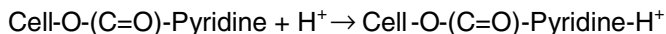
McIlroy and Lewis<sup>94</sup> reacted cotton with nicotinoylthioglycollate (NTG) which was prepared in high yields from the reaction of sodium thioglycollate



9.51 Amino derivatives of NMA-treated cotton.



9.52 Comparison of colour yields obtained for dyeings of C.I. Reactive Red 5 (2% o.w.f.) on various aminopropionamido-methylene-oxycelluloses ( $\text{Cell-O-CH}_2\text{-NH-CO-CH}_2\text{CH}_2\text{NR}_1\text{R}_2\text{R}_3$ ).



9.53 NTG modified cellulose.

with nicotinoyl chloride at pH 8.0 (0–5°C). NTG was applied to cotton fabric by a pad-dry-bake (typically pH 8.0, 180°C for 60 s) procedure to produce the modified cellulose shown in Fig. 9.53.

It was found that a bis-MCT dye (C.I. Reactive Red 120) could be dyed, at 2% dye o.m.f., on this substrate from a boiling dyebath set at pH 3.0, in the absence of the usually added electrolyte, to give an overall fixation efficiency of 65% – untreated cotton dyed in this manner gives an efficiency of zero (the traditional salt alkali procedure to apply this dye to untreated cotton gave a fixation efficiency value of 74%).

## 9.6.2 Reactive fibres rather than reactive dyes

Existing reactive dye systems depend on two basic elements:

1. an electron-deficient ‘reactive’ carbon centre in the dye
2. an electron-rich ‘nucleophilic’ centre in the fibre.

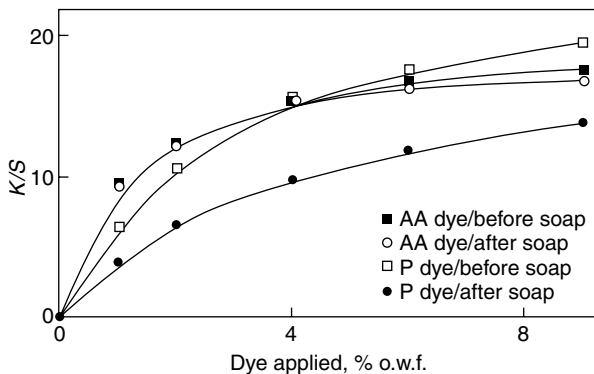
The above concept may be reversed by producing dyes containing pendant nucleophiles. Aminoalkyl dyes are conveniently prepared from the reaction of aliphatic diamines with existing reactive dyes.

Reactive cellulosic fibres may be prepared by the following methods:

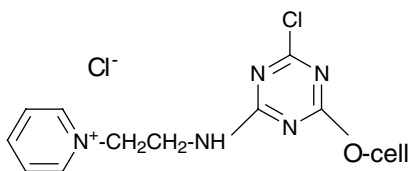
### (i) Reaction of cotton with NMA

It was shown<sup>95</sup> that the aminoethylamino-*s*-triazinyl dye, prepared from the reaction of C.I. Reactive Red 58 (Procion Red H8BN-ICI) with ethylene-diamine, gave excellent colour yields when applied to NMA activated cotton at pH 10.5 in the presence of 80 g/L salt (Dye AA). Typical results are reproduced in Fig. 9.54; this figure also shows colour yield (K/S) versus dye applied, before and after soaping, for the unchanged parent monochlorotriazine dye applied to untreated cotton by the recommended reactive dyeing procedure (Dye P).

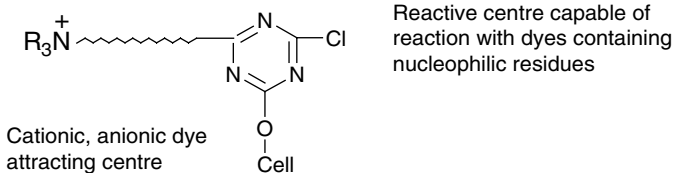
Figure 9.54 demonstrates that practically *no dye* is removed from the activated cotton, even when soaping at the boil (15 min) in an aqueous solution of non-ionic detergent (5 g/L) and sodium carbonate (2 g/L). The comparative result, achieved with unmodified C.I. Reactive Red 58 on untreated cotton, indicated that up to 30% of non-reacted dye is removable during the soaping procedure. Thus dyeing activated cotton with aminoalkyl dyes offers significant potential savings, since on the basis of these results the soaping process could be omitted.



9.54 Build-up curves for C.I. Reactive Red 58 (P dye) on untreated cotton and its aminoethyltriazine (AA dye) on NMA cotton.



A simplified representation of this substrate is:

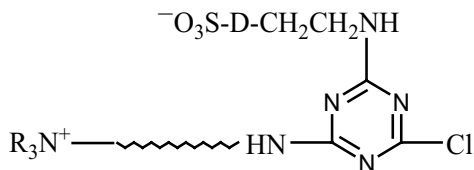


9.55 DCPEAT activated cotton.

- (ii) Reaction of 2,4-dichloro-6-(2-pyridino-ethyl-amino)-*s*-triazine (DCPEAT) with cotton

In an attempt to improve substantivity in the no-salt dyeing system, a novel compound, DCPEAT has been studied by Lewis and Lei.<sup>95</sup> If this compound were to be applied and fixed on cellulosic substrates under well-defined conditions the modified substrate shown in Fig. 9.55 would be produced.

This reactive substrate shows excellent dye-fibre fixation when it is dyed with aminoalkyl dyes (Fig. 9.56). DCPEAT contains two reactive chlorine



9.56 Aminoalkyl dye – DCPEAT cotton reaction product.

atoms – when applied to cellulosic substrates under weakly alkaline conditions one of the chloro substituents is displaced, leading to covalent fixation. The cellulosate substituent deactivates the triazinyl ring, ensuring that the product of the pre-treatment reaction contains significant numbers of MCT residues. Since aliphatic amino is a more powerful nucleophile than cellulose hydroxyl, very efficient reaction of the dye at the monochlorotriazine residue should be possible during subsequent dyeing with aminoalkyl dyes.

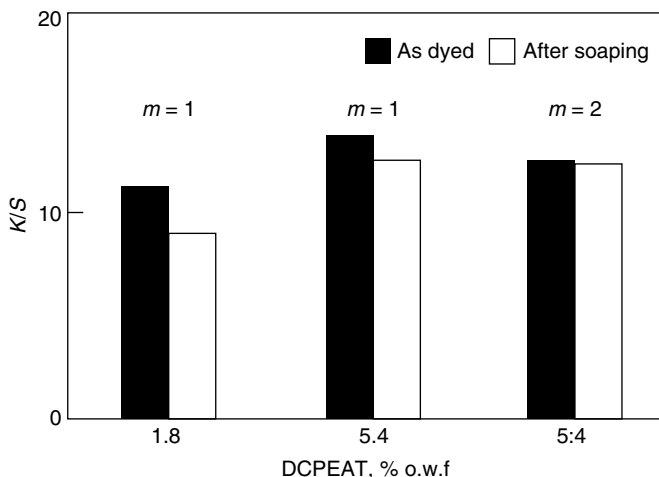
It was found that the DCPEAT modified substrate was best prepared by a pad-batch cold (24 h) technique at pH 8.5, followed by a thorough cold water wash-off. Although long-liquor applications of DCPEAT were studied, inadequate substantivity of this compound for the fibre gave poorer subsequent dyeings than those obtained on pad-batch prepared substrates.

Two aminoalkyl dyes were employed to dye this modified substrate in the absence of salt, viz:

Procion Red H8BN – monoaminoethyl-aminotriazine derivative and Procion Red HE-3B (C.I. Reactive Red 120) – bis(aminoethyl-aminotriazine) derivative.

The results obtained when dyeing these two nucleophilic dyes ( $m = 1$ ,  $m = 2$ ) on the above substrate are shown in Fig. 9.57 (dyeing conditions: no salt, pH 9.0, dye – 2% o.m.f., raise to the boil, boil 1 h). This figure demonstrates that good substantivity and fixation are achieved at the higher levels of DCPEAT application (5.4% o.m.f.); slightly better results were achieved using the bifunctional aminoethyl dye ( $m = 2$ ) derived from C.I. Reactive Red 120.

Tosylation of cotton is an old method to activate cotton to make a reactive fibre and was first developed by Karrer and Wehrli<sup>96</sup> in 1926; in this case amination was used to displace the tosyl group and thus render the fibre dyeable with anionic ‘acid’ dyes. Arrowsmith and Lewis<sup>97</sup> found that tosylated fibres would react very efficiently with dyes containing nucleophilic centres; surprisingly hydrolysed vinylsulphone dyes (hydroxyethylsulphone



9.57 Colour yields of aminoethylamino-*s*-triazine nucleophilic dyes applied to DCPEAT modified cottons.

dyes) could be dyed at 2% depth on tosylated cotton, without salt, from boiling pH 8.0 baths, to give fixation efficiencies of 76%.

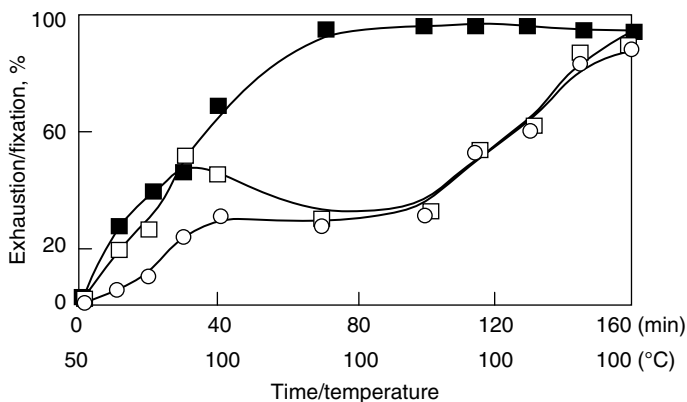
### 9.6.3 Covalent bonding of nucleophilic dyes on fibres using cross-linking systems

The earliest commercial success in this area was achieved by BASF with the Basazol system.<sup>98,99</sup> In this case dyes containing pendant nucleophilic groups were fixed to cellulose hydroxyl residues using a tri-functional cross-linking agent 1,3,5 – triacroylamino-hexahydro-*s*-triazine (Fixing Agent P). The dyes employed contained sulphonamide residues which were sufficiently nucleophilic above pH 10.5 to undergo Michael addition with the activated double bonds of the cross-linker. In fact, many of the aminosulphonyl dyes selected as Basazol dyes were already available as 2:1 pre-metallised dyes for dyeing wool (Ortolan – BASF). The simplified scheme shown in Fig. 9.58, describing the covalent fixation of the sulphonamide dye to cotton is relevant, although it should be noted that Baumgarte<sup>98</sup> describes up to nine possible reaction products from such a system.

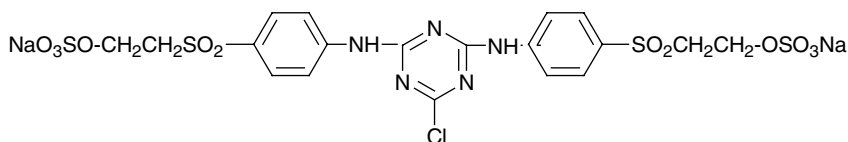
Clearly the above species contains an unreacted double bond which is capable of undergoing further reaction with either the nucleophilic sulphonamide residue or with the nucleophilic cellulosate anion. This system was highly novel, but this dye range was withdrawn from the market because







9.59 Exhaustion/fixation curves from wool dyed by the aminoalkyl dye/FAP method, using 4% o.w.f. bisaminoalkyl dye.



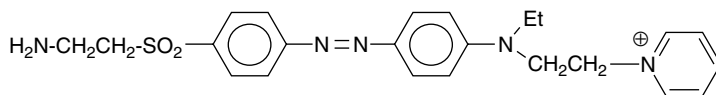
9.60 The tri-functional cross-linker, XLC.

cross-linking agent. Very high exhaustion values were obtained and fixation values of 95% were recorded. This system had the advantage of low reactivity until the boil was reached, giving the dye an excellent opportunity to level before covalent bonding became significant. Typical exhaustion/fixation results from the aminoethylamino-*s*-triazine dye/triacrylamino-hexahydro-*s*-triazine (FAP) system are shown in Fig. 9.59.

Lewis, Wang and Lei also studied the use of a bifunctional cross-linking agent, methylene-bis-acrylamide, to fix aminoalkyl dyes on wool.<sup>103</sup>

If such systems are to be further developed for covalently fixing dyes on cellulosic materials, the Basazol experience appears to indicate that fibre-substantive cross-linking agents should be developed along with suitably nucleophilic dyes. Another system<sup>104</sup> has described the promising covalent fixation to cellulose of sulphonated chromophores containing pendant aminoalkyl groups by reaction of the dye and the cellulose with the cross-linking agent, disodio-2-chloro-4',6-di(aminobenzene-4-sulphatoethylsulphone)-*s*-triazine (XLC) (Fig. 9.60).

This agent (XLC) has also been investigated as a cross-linking agent to covalently fix amino-nucleophile containing dyes to nylon<sup>105,106</sup> and wool<sup>107</sup>



9.61 Amino-ethylsulphone cationic dye.

substrates. In the case of wool, a very high degree of covalent fixation was recorded, either by co-applying dye and cross-linker at pH 6.0 (100°C) or by dyeing first and then adding the cross-linker to the exhausted bath. Nylon, owing to its paucity of nucleophilic amino sites, represented a bigger problem. However, promising results were obtained by synthesising the aminoalkyl cationic dye shown (Fig. 9.61) and applying it to nylon at pH 9.0 at the boil.<sup>108</sup> Subsequent after-treatment, at the boil, with XLC resulted in promising levels of dye–fibre covalent bonding, even in deep shades.

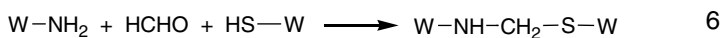
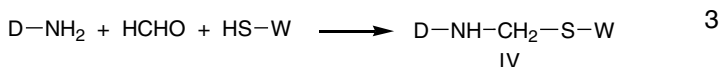
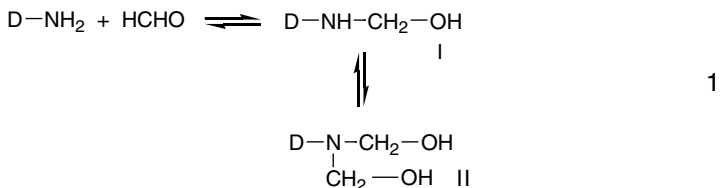
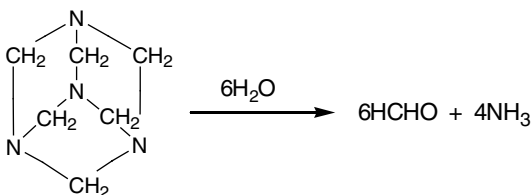
Surprisingly cyanuric chloride<sup>109</sup> has been proposed as a cross-linking agent for fixing dyes containing pendant amine groups to cellulosic fibres. Clearly from a health and safety point of view this approach is flawed; cyanuric chloride is a primary skin irritant and is known to cause severe allergic reactions in certain individuals.

Lewis, Lei and Wang<sup>110</sup> proposed a very simple cross-linking system to fix aminoalkylamino-*s*-triazine dyes on wool, based on hexamethylene tetramine (or hexamine). This agent was co-applied to wool with nucleophilic dyes at pH 5.0 and at the boil, and found to promote covalent fixation of the dye to the fibre. Hexamine breaks down under such conditions, to produce formaldehyde, which is the active cross-linking species. Since covalent fixation does not commence until the boil is reached, the dyes have an excellent opportunity to migrate and produce level dyeings.

Figure 9.62 describes the various possible reactions in this fixation process – product 3 is believed to be responsible for the excellent fixation properties of the dyeing since this dye–fibre bond is not reversible.

## 9.7 Conclusions

Reactive dyes and other systems which form covalent dye–fibre bonds have been described. It is evident that this technology offers the colourist many options for producing full bright and tertiary shades on cellulosic and polyamide fibres. Commercially available products are, as yet, deficient in the full-shade area on cotton and nylon since their build-up is limited due to the fixation of sulphonate groups imparting a large negative charge which repels anionic dye molecules. In such fields as African prints on cotton, it is necessary to dye full, bright shades, as deep as 8% o.m.f., and in this case



#### 9.62 Reactions of hexamine with amino dyes and wool nucleophiles.

current reactive dyes do not perform adequately, giving weaker than desired shades and requiring intensive washing-off to achieve the required washing fastness. Furthermore, in long-liquor dyeing, the use of large quantities of inorganic electrolytes is increasingly viewed as environmentally unfriendly and thus the development of new systems using minimal salt without sacrificing level dyeing properties is desirable.

In the light of the above, there is still great scope for further research and development to maximise the benefits of reactive dye systems; even so the development and use of reactive dyes, has to rate as one of the most important achievements of colour chemists.

## 9.8 References

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**Abstract:** This chapter traces the history of the evolution of disperse dyes and their growth over the last 80 years. These dyes were originally synthesised for the dyeing of cellulose acetate fibres and subsequently found to be suitable for the dyeing of a large number of synthetic fibres, particularly polyester fibres. Initially, the 'cellulose acetate' dyes were modified to improve their sublimation and gas-fume fading fastness to make them suitable for the dyeing of polyester. Later on, the dyes suitable for the dyeing of polyester were specifically invented, which included alkali-clearable dyes and dyes with low thermomigration and high wash fastness. In the beginning, the dyes were classified on the basis of their sublimation fastness, however, nowadays they are being grouped and created on the basis of end use such as dyes for automotive fabrics, high-visibility garments, polyester-cellulose blends, sportswear, discharge, ink-jet and transfer printing. Efforts are being taken to invent dyes for dispersant-free dyeing so as to minimise the pollution caused by the dyeing of disperse dyes on polyester and other substrates.

**Key words:** sublimation fastness, thermomigration, alkali-clearable dyes, high-visibility dyes, dyes for sportswear, dispersant-free dyes, dyes for ink-jet printing, discharge printing, transfer printing and dyes for automotive fabrics.

## 10.1 Introduction

Disperse dyes today constitute the second largest sector in the dyeing industry: in 2006, 125 thousand tons of disperse dyes were produced, with a value of US\$900 million.

The growth of disperse dyes is closely related to the growth of polyethylene terephthalate (PET) and to the development of two new fibres which can be disperse-dyed: firstly, a new polyester, polytrimethylene terephthalate (PTT), known as Corterra<sup>®</sup>, developed by Shell and licensed by KoSa; and secondly, Nature Works polylactic acid (PLA), developed by a joint venture between Cargill and Dow.

Disperse dyes are also used for the colouration of nylon, where their main attribute is their ability to cover barré defects, but their somewhat limited fastness properties restrict their use to shades of pale and medium depths.

Disperse dyes are also used for dyeing acrylic fibres, on which they have very good light fastness, but their use is restricted to pale shades because of their limited build-up properties. Other fibres such as polypropylene, are

often mentioned in disperse dye patents, but these are generally of academic interest only and are not used for practical applications.

### 10.1.1 Evolution of disperse dyes from cellulose acetate dyes

The invention of disperse dyes in 1923–24 confirms the old adage ‘Necessity is the mother of invention’, as they were developed to solve the problem of dyeing cellulose acetate, the first hydrophobic fibre, by creating a fine dispersion of sparingly soluble dyes. The dyes were initially known as cellulose acetate dyes; later, however, they were found to be suitable for dyeing a wide variety of fibres and in 1953 the Society of Dyers and Colourists renamed them ‘disperse dyes’ (Baldwinson, 1961). The Society also recommended that the term *disperse dyes* should mean: ‘a class of water-insoluble dyes originally introduced for dyeing cellulose acetate, and usually applied from fine aqueous suspensions’. To quote Fourness (1956), without disperse dyes and the disperse technique, ‘many man-made prodigies would have been stillborn, or at best remained Peter Pans’.

The first ever disperse dye, SRA Orange 1, was synthesised in 1923 by Holland Ellis for British Celanese Ltd, for use in dyeing cellulose acetate fibres. However, the Gold Medal of the Society of Dyers and Colourists was awarded to Baddiley and Shepherdson for introducing ‘Duranol’ dyes in 1924 (Fourness, 1974). Subsequently, disperse dyes were developed to meet the specific requirements of polyester: these included ‘alkali-clearing’ dyes, and dye with low thermo-migration and high wet fastness and so on.

The traditional classification of disperse dyes on the basis of sublimation characteristics (i.e. A, B, C, D or E, SE, S) and concomitant energy levels (low, medium, high) has undergone considerable change. The first such change occurred when the concept of ‘rapid dyeing’ (RD) was introduced in the 1980s, whereby both ‘on-tone’ dyeing and dye compatibility arising from their concentration-based exhaustion behaviour were desirable. This led to the emergence of RD dyes produced from multiple dyes, as well as compatible trichromatic dyes based on a single dye. More recently, dyes have been classified on the basis of their end-use, for example: dyes for automotive fabrics with very good light fastness; dyes for sportswear and heavy-duty work-wear with excellent wash fastness; luminous disperse dyes for high-visibility garments used by traffic controlling personnel; and compatible dyes for home-textiles with good levelling properties, reasonable fastness and so on. Various other minor classifications also exist, such as dyes suitable for solvent dyeing, and  $\text{ScCO}_2$  dyeing, among others.

Disperse dyes were originally introduced as pastes, which posed problems including settling and crust formation. Subsequently spray drying was introduced; in this method a finely ground mixture of dispersing agent and dye was

spray dried to obtain self-dispersible powders. The automation of the dyeing process again led to the production of easily 'pumpable' liquid dyes. After easy dispersibility and pourability, the most important factor in dye production is the particle size, since the solubility of the dye is directly proportional to the particle size and hence to its ultimate exhaustion on polyester. A typical dye may have a particle size of between 0.1 and 1  $\mu\text{m}$ ; some may be nanoparticles.

## 10.2 Developments in disperse dyes

The introduction of Terylene, a new polyester fibre, in 1949, gave new impetus to the development of disperse dyes. These developments are discussed in the following sections.

### 10.2.1 Modification of cellulose acetate dyes

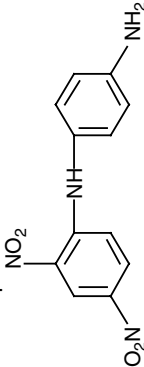
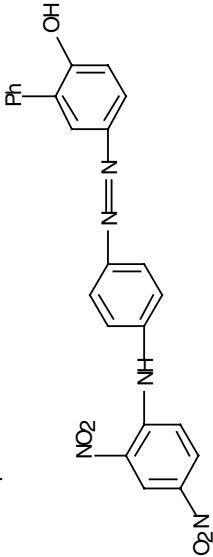
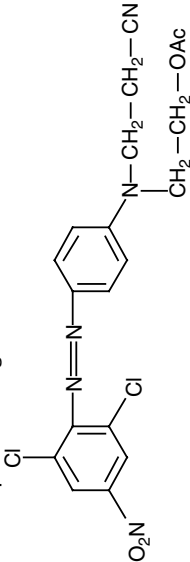
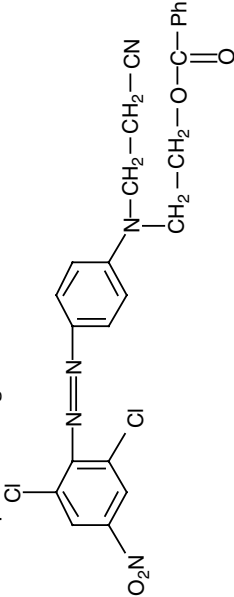
Disperse dyes – simple, nitro, azo and anthraquinone dyes – were found to have low sublimation fastness; those based on anthraquinones were found to fade when exposed to nitrogen oxides commonly found in urban environments.

The first task in the development of suitable disperse dyes for the dyeing of polyester and other synthetic fibres was the modification of the available dyes with the aim of improving their sublimation and gas fume fading properties.

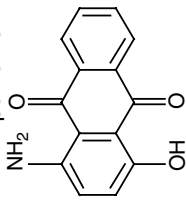
The sublimation fastness of dyes is particularly important in the dyeing of polyester fibres, since polyester fabrics are heat-set at close to 200°C. Improvements in the sublimation fastness have been achieved through the introduction of additional polar groups or by increasing the molecular size of the dye. Many examples of the modification of the original cellulose acetate dyes to improve their sublimation fastness have been discussed by Dawson (1983, 1984, 1991). In almost all cases the improvement in the sublimation fastness has been achieved by increasing the molecular size of the original dye, as illustrated in Table 10.1.

The second of the shortcomings mentioned above, the tendency of some anthraquinones to fade on exposure to oxides of nitrogen, was discovered soon after the introduction of cellulose acetate dyes. The susceptible anthraquinone dyes contain an amino group that includes most of the blues, some violets, and some reds; oxides of nitrogen cause fading in these dyes due to diazotisation or to N-nitrosamine formation. The ease with which this fading occurs varies considerably according to the constitution of the dye, and appears to be dependent upon how basic the dye is and/or upon the protective influence of groups in positions adjacent to the sensitive basic group (Rowe and Chamberlain, 1937). Many such dyes that exhibit fading in the presence of nitrogen oxides have been phased out. For instance, C.I. Disperse Violet 1 (Fig. 10.1), i.e. 1, 4, diaminoanthraquinone, used for the dyeing of a bright violet shade on cellulose acetate and polyester, has been replaced by C.I. Disperse Violet 27 (Fig. 10.2). However, these dyes have now been replaced by dyes with improved sublimation fastness.

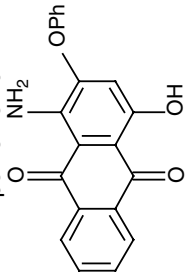
Table 10.1 Improving sublimation fastness of disperse dyes by increasing molecular size

Original dye with low sublimation fastness	Modified dye with improved sublimation fastness
<p>C.I. Disperse Yellow 9</p> 	<p>C.I. Disperse Yellow 70</p> 
<p>C.I. Disperse Orange 30</p> 	<p>C.I. Disperse Orange 62</p> 

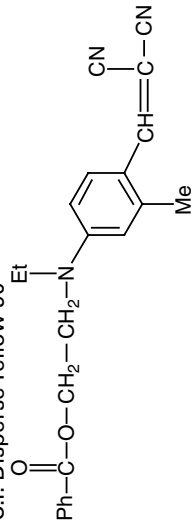
C.I. Disperse Red 15



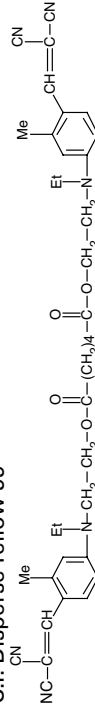
C.I. Disperse Red 60

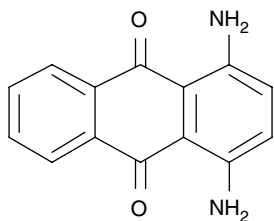


C.I. Disperse Yellow 90

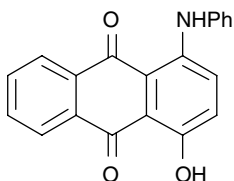


C.I. Disperse Yellow 99

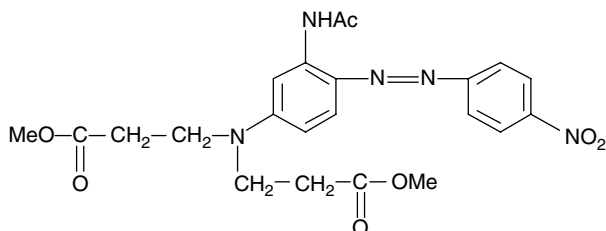




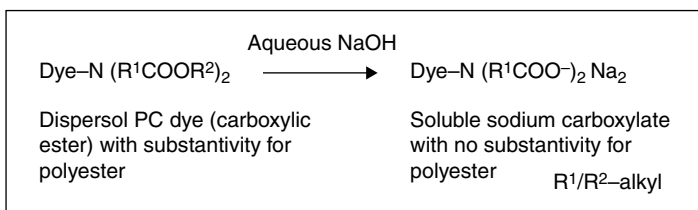
10.1 C.I. Disperse Violet 1.



10.2 C.I. Disperse Violet 27.



10.3 C.I. Disperse Red 278 (Dispersol Red 4G-PC).



10.4 Alkaline hydrolysis of Dispersol PC dyes.

## 10.2.2 Dyes developed specially for dyeing of polyester

### *Alkali-clearable dyes*

Alkali-clearable disperse dyes were introduced in 1976 by ICI for the purpose of exhaust dyeing polyester cellulosic (PC) blended fabrics, and were marketed as Dispersol PC dyes. These are azobenzene disperse dyes containing alkoxy carbonyl groups, such as C.I. Disperse Red 278 (Dispersol Red 4G-PC)



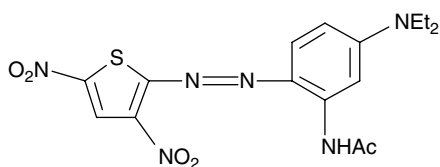
(Fig. 10.3). In the presence of an alkali the alkoxycarbonyl groups are hydrolysed to the corresponding carboxylic acids (Fig. 10.4), which give the dye water solubility but little or no substantivity for cellulose or polyester fibres.

These dyes were found to be particularly useful in the printing of polyester/cellulose blends in conjunction with a conventional reactive dye. Using this method, the dye is hydrolysed during the alkaline wash-off process carried out to remove unfixed reactive dyes and thus does not stain adjacent white areas. These dyes avoided the need for sodium hydrosulphite in the post-treatment of dyed/printed fabrics and significantly reduced the cost of reduction clearing as well as that of effluent treatment. This unique property has also been exploited in the production of discharge prints on polyester fabrics.

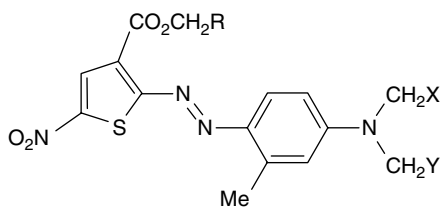
In 1977 ICI introduced thiophene-based disperse dyes such as C.I. Disperse Green 9 (Dianix Green CC) (Fig. 10.5). These dyes decompose during the alkaline after-treatments performed on dyed fabrics to produce colourless or only slightly tinted decomposition products. Thiophene-based disperse dyes were first reported in 1949; they were subsequently extensively investigated and patented by Dickey *et al.* (1958) and commercialised by Eastman Kodak.

A series of blue monoazo thiophene-based disperse dyes containing carboxylic acid ester groups (Fig. 10.6) have been synthesised in the search for colourants with high fastness and reduced environmental impact (Choi *et al.*, 1999). The dyeings produced by applying these dyes to polyester were found to be alkali clearable. Depending on the dye, the depth of shade and the use of thermosetting, alkali clearing was observed to be as effective, or almost as effective, as a reduction clear.

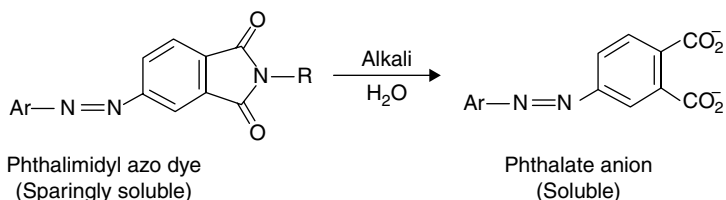
The advent of alkali-clearing disperse dyes that incorporate diester or thiophene groups within the structure enabled highly productive one-bath,



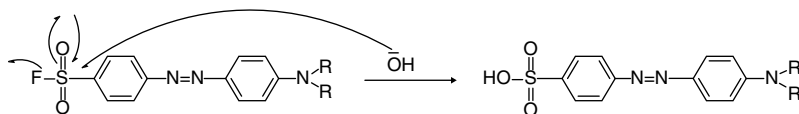
10.5 C.I. Disperse Green 9 (Dianix Green CC).



10.6 Blue monoazo thiophene-based disperse dyes containing carboxylic acid ester groups.



### 10.7 Alkali hydrolysis of phthalimide-based azo disperse dyes.



### 10.8 Reaction mechanism of the hydrolysis of dyes in alkali medium.

two-stage processes introduced for the exhaust dyeing of polyester/cellulosic blends, as exemplified by ICI's New Select Process.

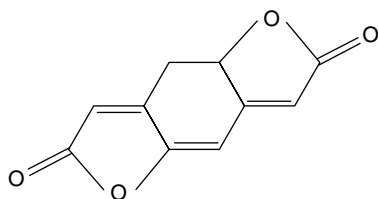
More recently, phthalimide-based alkali-clearable dyes have been reported (Choi *et al.*, 2007; Koh and Kim, 1998; Koh *et al.*, 2008, 2009). These dyes contain a phthalimide moiety, undergo ring opening and conversion to water-soluble products under relatively mild alkaline conditions (Fig. 10.7). One advantage of these dyes is the lack of azo bond reduction, which can lead to harmful primary aromatic amine-containing compounds.

Another set of alkali-clearable dyes being investigated is based on azo disperse dyes containing a fluorosulfonyl group. An azo disperse dye incorporating a fluorosulfonyl group is hydrolysed under relatively mild alkaline conditions and temperature to a dye containing a water-solubilising sulphonate group, without cleavage of the azo bond as shown in Fig. 10.8 (Parvizi *et al.*, 2009).

There are increasing global legislative pressures to reduce the impact of dyeing processes on the environment through reductions in effluent discharge as well as in the use of energy and materials. Alkali-clearable disperse dyes offer a means of tackling both of these challenges simultaneously.

### *Dyes with low thermo-migration properties*

Thermo-migration is the phenomenon of the diffusion of dye from the fibre interior to the fibre surface during heat-setting. Thermo-migration of disperse dyes has been attributed to the breakage of the interaction between dye and fibre as a result of increased thermal motion of both the dye molecule and the polymer chain at elevated temperatures. The problem of thermo-migration becomes more severe as the denier of fibre decreases, and it is regarded as the source of the low wash fastness exhibited by some disperse dyes. Factors affecting thermo-migration are known to be the fibre thickness, the chemical structure of the disperse dye, the amount of absorbed dye in the fibre, and



10.9 Benzodifuranone.

heat-setting conditions. The effects of thermo-migration are also accelerated by the application of fabric finishes, such as fluorocarbon after-treatments.

Research into disperse dyes with a low tendency towards thermo-migration high wet fastness properties resulted in the discovery of benzodifuranone (Fig. 10.9) during the mid-1970s by C W Greenhalgh, recipient of the Society of Dyers and Colourists (SDC)'s Perkin Medal in 1992 (Greenhalgh *et al.*, 1994). Benzodifuranone-based dyes can withstand the most severe after-treatments with negligible effect on the subsequent wet fastness of the dyed fabrics.

ICI subsequently introduced disperse dyes based on benzodifuranone such as Dispersol Red CBN (C.I. Disperse Red 356) in 1985, Brilliant Scarlet D-SF (C.I. Disperse Red 367) in 1989 and Dispersol Brilliant Red DSF in 1992. Some of the Terasil WW disperse dyes developed by Ciba, Dianix XF/SF of DyStar are based on benzodifuranone chromophoric.

Colourants based on benzodifuranone and methane chromophores have become technically important for the colouration of polyester and its cellulosic blends. They perform well on international standard and commercial wash fastness tests (such as ISO C06 C2S), which involve relatively high temperatures and alkaline wash liquors (Choi *et al.*, 1999).

## 10.3 Types of disperse dye

### 10.3.1 Rapid dyeing dyes for on-tone dyeing

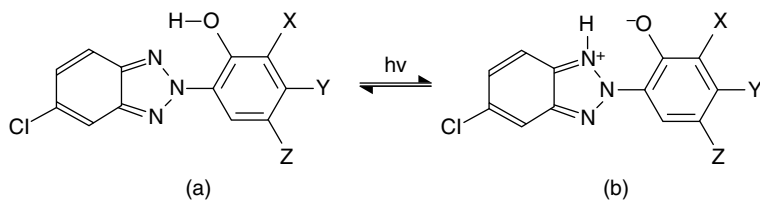
A sudden increase in the cost of dyeing after the energy crisis of the early 1970s led to the development of optimised dyeing processes, which required less time and consequently less energy consumption. The reduction in dyeing time required that the dyes used in the mixture must exhaust simultaneously in order to produce on-tone dyeing. The search for dyes with near-identical exhaustion profiles led to the development of new methods of assessing the compatibility of dyes, followed by the shortlisting of dyes into compatible groups. The tests used to assess the compatibility are the 'Dip Test' of du Pont and the 'V-number' system of YCL and Mitsui. The dyes that have been found to be sufficiently compatible for most purposes irrespective of the proportions in which they are mixed are a trichromatic combination of C.I.

Disperse Yellow 54, C.I. Disperse Red 60 and C.I. Disperse Blue 56, or a combination of C.I. Disperse Yellow 64, C.I. Disperse Red 60 and C.I. Disperse Blue 56 (Baldwinson, 1985). On-tone dyeing has also been achieved by using specially prepared mixtures of 'primary dyes' sometimes referred to as RD dyes. An individual RD dye is made up of a mixture of rapid and slow dyeing components of the same hue. For instance, a Yellow RD dye may contain 3–4 yellow dyes with a varying range of exhaustion profiles. Thus in combination shades there may be 10–12 individual dyes of different hue and exhaustion profiles in the dye bath, ensuring on-tone dyeing.

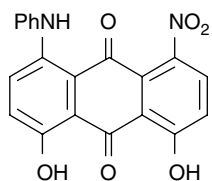
### 10.3.2 Dyes for automotive fabrics

Automotive fabrics are often exposed to heat and light for long periods, with fabric temperatures in a locked car rising as high as 100°C in summer in many countries. The combined effects of light and heat can lead to accelerated fading; hence, more stringent fastness tests such as EN ISO 105-B06 and DIN 75202 (FAKRA) have been developed to assess the fastness of dyes used for the colouration of automotive fabrics. Initially, a combination of a disperse dye with a ultraviolet (UV) absorbers, such as Tinuvin P 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, was used to achieve the required fastness standards (Kehayoglou and Tsatsaroni, 1993). Subsequently, dyes containing a hydroxybenzotriazole moiety were proposed. Hydroxybenzotriazole photostabilisers, such as Fig. 10.10a, absorb UV light and dissipate the energy by undergoing excited state intramolecular proton transfer (Fig. 10.10a to b), followed by ground state proton transfer (Fig. 10.10b to a) were synthesised and investigated by Freedman *et al.* (Freeman and Posey, 1992), (Freeman, 1995). Improvements have been reported in the light fastness of some dyes such as C.I. Disperse Red 167 and C.I. Disperse Yellow 86 when a UV absorber is incorporated into the dye structure (Freeman *et al.*, 1999).

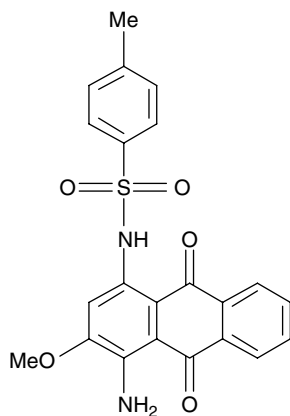
However, the light fastness of inherently light fast dyes (those with a light fastness of seven or above) such as C.I. Disperse Blue 77 (Fig. 10.11), C.I. Disperse Red 86 (Fig. 10.12) and C.I. Disperse Yellow 42 (Fig. 10.13) is not affected by the addition or incorporation of UV absorbers. The high light fastness exhibited by anthraquinone dyes such as C.I. Disperse Red 60 (Fig.



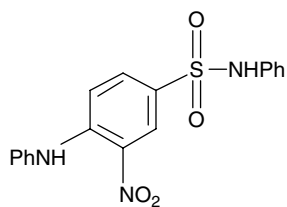
10.10 Hydroxybenzotriazole photostabilisers.



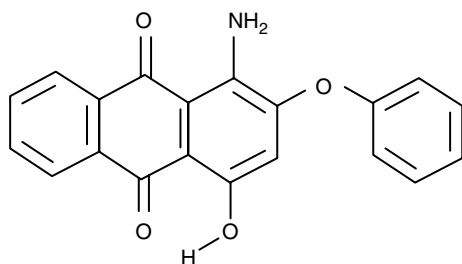
10.11 C.I. Disperse Blue 77.



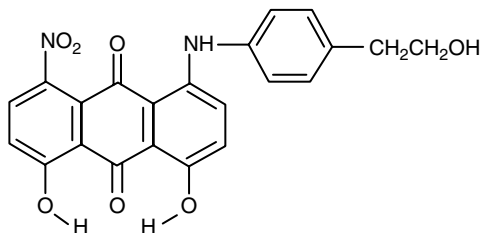
10.12 C.I. Disperse Red 86.



10.13 C.I. Disperse Yellow 42.



10.14 C.I. Disperse Red 60.



10.15 C.I. Disperse Blue 27.

10.14), C.I. Disperse Blue 27 (Fig. 10.15) and 77 having an  $-OH$  group in  $\alpha$ -position of the anthraquinone ring, has been attributed to the intra-molecular proton transfer from the  $-OH$  group to the adjacent  $C=O$  group on exposure to light. Thus the energy absorbed by the dye molecule is dissipated in the form of heat (Freeman *et al.*, 2004). Likewise the high light fastness of C.I. Yellow 42 may be attributed to the hydrogen bonding between the azo bond and the adjacent  $-NO_2$  group.

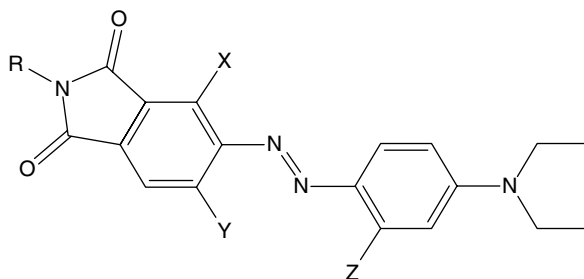
Beside these dyes, the other disperse dyes recommended for the colouration of automotive fabrics are Disperse Yellow 163, Disperse Red 92, Disperse Red 86, Disperse Violet 28, Disperse Blue 60, Disperse Red 279, Disperse Red 302, and mixtures of the above.

### 10.3.3 Dyes for sportswear

Sportswear needs to be washed frequently, and hence dyes with very high wash fastness should be used. The dyes used for the colouration of sportswear must meet stringent criteria relating to wash and perspiration fastness, as per the test methods recommended by American Association of Textile Chemists and Colorists (AATCC) and International Organization for Standardization (ISO), and in some cases client-recommended methods such as: AATCC IIA Fastness to washing 49°C, ISO 105-C06 C2S Fastness to washing 60°C, ISO 105-E01 Fastness to water, ISO 105-E04 Fastness to perspiration, M&S C4A Fastness to washing 50°C, Adidas Fastness to washing 40°C, Puma Fastness to washing 40°C and Nike Fastness to washing 50°C.

According to Cunningham (1996) two important determinants of the wash fastness of goods coloured with disperse dyes are the efficiency of the post-dyeing clearing process in removing surface dye and the extent of thermal migration of dye caused by heat treatments during finishing.

Phthalimide-derived dyes that can be effectively eliminated from the surface of the dyed substrates (see Section 10.2.2) through simple alkali treatment have been exploited commercially as a means of meeting the increasingly demanding specifications for wash fastness of textiles. The Dispersol XF range of dyes developed by ICI in the 1970s relied on this



10.16 Blue dicyano and orange dibromo derivatives of phthalimide.

approach to achieve high wash fastness (Choi *et al.*, 2008a). Terasil® WW, Terasil® W-EL (Ciba) and Foron®SWF (Clariant) are other commercial dye ranges that include products based on alkali-clearable dyes.

In another study, Choi *et al.* (2008b) reported that the blue dicyano and orange dibromo derivatives of phthalimide (Fig. 10.16) show better wash fastness than their red parent dyes, due to the proximity of electron-withdrawing groups to the phthalimide ring system, increasing the propensity of the latter towards hydrolysis to a more soluble phthalate species during clearing and laundering. This is likely to inhibit staining by lowering the amount of surface dye and partitioning dye towards the wash liquor.

Moreover high-washfast phthalimide-based azo disperse dyes can be easily removed by an alkaline after-wash rather than with reductive clearing, which is harmful to the environment because of its high biological oxygen demand (BOD). These dyes can therefore be considered to be environmentally friendly (Koh *et al.*, 2009).

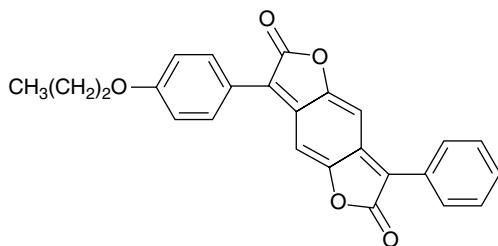
Another example of increased susceptibility to alkali being employed advantageously is the use of benzodifuranone chromophore, which was commercialised in the 1980s. Benzodifuranone dyes produce bright red shades with high wash fastness. However, the lactone group in these dyes is susceptible to hydrolysis by alkalis (Greenhalgh *et al.*, 1980). This is most useful when this type of disperse dyes are applied to polyester: the dyeings produced are readily alkali-cleared, because the chromophore is discharged by alkali to a colourless compound.

Dyes based on benzodifuranone chromophore, such as C.I. Disperse Red 356 (Fig. 10.17), also have low thermo-migration properties (see Section 10.2.2).

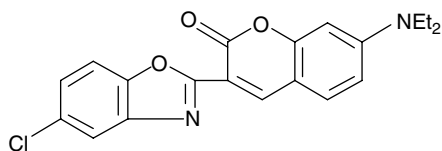
Some benzodifuranone dyes that have very high wash fastness are sold under the trade name Terasil® WW (Ciba) and Dianix® XF/SF dyes.

#### 10.3.4 High visibility dyes – fluorescent dyes

Fluorescent disperse dyes are used for the colouration of polyester fabrics required for the production of high-visibility safety garments. The



10.17 C.I. Disperse Red 356.



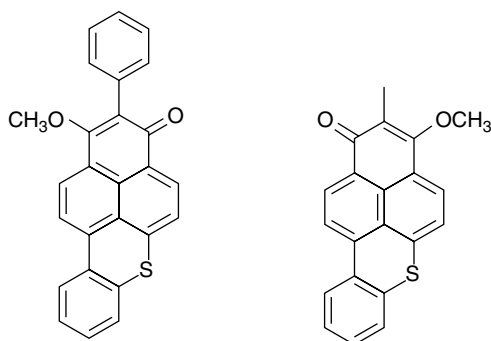
10.18 C.I. Disperse Yellow 232.

performance of these garments is evaluated according to the EN 471:1994 standard. This standard outlines the requirements for textiles dyed with fluorescent dyes that are produced for the manufacture of high-visibility 'warning' clothing. This type of high-visibility garment is manufactured in only three colours: yellow, orange and red. Fluorescent disperse yellow dyes with C.I. numbers 82, 184, 186 and 232 belong to the coumarin group of dyes while C.I. Disperse Yellow 199 dye belongs to the benzoxanthone derivatives (Szuster *et al.*, 2004).

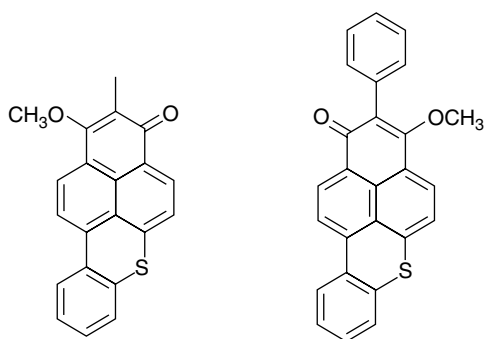
The first fluorescent dyestuffs for polyester fibres appeared towards the end of the 1960s. These were coumarin derivatives, which contain an electron-releasing group in the 7-position of the coumarin ring such as an N,N-diethylamino group and a heterocyclic electron-acceptor residue, in the 3-position, such as C.I. Disperse Yellow 232 (3-(5-Chloro-2-benzoxazolyl)-7-(diethylamino)-2H-1-benzopyran-2-one) (Fig. 10.18) (Christie, 1993). These were called 'Shock Colour'. Commonly used coumarin dyes are yellow with a green fluorescence, and attempts have been made to synthesise red coumarin dyes (Moeckli, 1980). Recently a series of coumarin dyes derived from arylsulphonation of the parent benzothiazole, benzimidazole and benzoxazole dyes have been synthesised and successfully applied to polyester fabrics to give fluorescent greenish-yellow shades with improved fastness to sublimation, washing and perspiration (Christie *et al.*, 2008).

Disperse Red 277 is the only fluorescent red dye that is currently in commercial use. During the 1970s Hoechst introduced some brilliant





10.19 Isomer used for production of C.I. Disperse Red 303.



10.20 Isomer used for production of C.I. Disperse Red 303.

fluorescent and light fast benzothioxanthenes, for use as disperse dyes for the dyeing of polyester in yellow, orange and bluish-red shades. C.I. Disperse Red 303, a mixture of isomers shown in Figs. 10.19 and 10.20 is one of the commercial yellowish-red dyes of this class.

### 10.3.5 Dyes for transfer printing

In the transfer printing process a disperse dye is printed onto a paper or foil support and is then heated in contact with the appropriate hydrophobic fabric at 160–220°C until the dye is transferred to the fabric, which usually takes about 20–30 s. Transfer printing requires the dye to sublime and to remain stable under the application conditions.

Ironically, the disperse dyes that were found to be unsuitable for normal printing were found to be appropriate for transfer printing and were reinvented for that purpose. The three ‘low energy’ disperse dyes that were

originally used were C.I. Disperse Yellow 54, C.I. Disperse Red 60 and C.I. Disperse Blue 14 (Dawson, 1983).

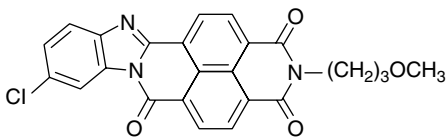
The most suitable dyes should: (a) have molecular weights between 240 and 340, (b) sublime in the region of 180–230°C, (c) have no affinity for the cellulose-based papers used as the print support, (d) be readily absorbed in the vapour state by most synthetic fibres, and (e) give adequate depth of colour and colour fastness properties on the fibres to be printed (Consterdine, 1976). Some commercially used dyes are C.I. Disperse Yellow 54, C.I. Disperse Orange 25, C.I. Disperse Red 1, C.I. Disperse Red 60, C.I. Disperse Red 375, C.I. Disperse Violet 8, C.I. Disperse Blue 3, C.I. Disperse Blue 14 and C.I. Disperse Blue 359.

### 10.3.6 Dyes for use with an alkaline bath

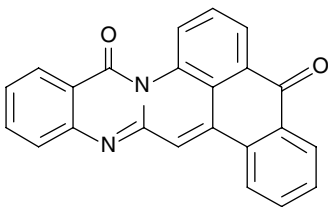
The dyeing of polyester from alkaline medium offers an opportunity to dye PC blends by a single bath, single-stage process. Most disperse dyes are adversely affected by heating in an alkaline bath; some select dyes have been found to be stable in an alkaline dyebath (pH 9.5), but these are much more expensive than conventional disperse dyes, so the demand for these dyes is relatively low.

The application of disperse dyes under alkaline conditions entails the use of a buffer that stabilises the bath and chelates the metal ions (Kazuhiisa *et al.*, 1993). The recommended buffers are mostly amino acid derivatives such as N,N-bis (hydroxyethyl) glycine in combination with sodium hydroxide.

Some of the yellow disperse dyes that are suitable for dyeing from an alkaline bath are C.I. Disperse Yellow 58 (Fig. 10.21), C.I. Disperse Yellow 63, C.I. Disperse Yellow 77 (Fig. 10.22), and C.I. Disperse Orange 32.



10.21 C.I. Disperse Yellow 58.



10.22 C.I. Disperse Yellow 77.

There are many alkali-stable red dyes based on anthraquinone chromophores, for example C.I. Disperse Red 60, C.I. Disperse Red 146, C.I. Disperse Red 191 and C.I. Disperse Red 207. However, not all anthraquinone-based dyes are suitable, so the dyes must be carefully selected: if a dye has a substitution group which is easily hydrolysed or ionised by alkali, it will not be stable for dyeing under alkaline conditions.

Violet to blue dyes with high alkali stability are C.I. Disperse Blue 54, C.I. Disperse Blue 73, C.I. Disperse Blue 77, C.I. Disperse Blue 87, C.I. Disperse Blue 197 and C. I. Disperse Blue 214. Black shades can be obtained by dyeing of a mixture of C.I. Disperse Blue 197 and C.I. Disperse Orange 45.

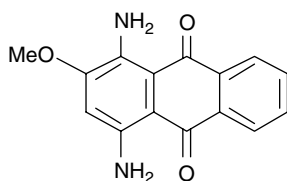
### 10.3.7 Dyes for discharge printing

Discharge printing of polyester to achieve fine prints on dyed grounds can be achieved by resisting the fixation of the dye by any of the following methods:

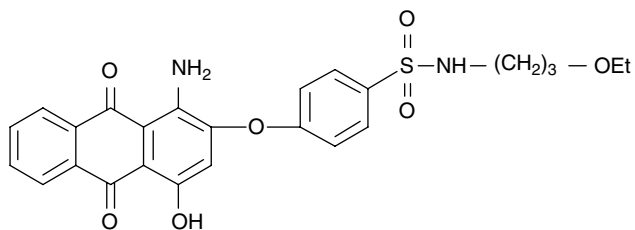
- (a) Use of a reducing agent
- (b) Formation of a metal-complex
- (c) Use of an alkali.

The process of discharge printing of polyester by using a reducing agent is a very well-established method and the dyes used as the ground shade, and as illuminating colours, are well-known, and can be accessed from any good shade-card.

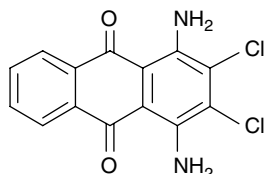
However, the second method of discharge printing makes use of the ability of certain disperse dyes to form chelation complexes with copper salts. The resultant 'metallised' disperse dye has little or no affinity for the polyester and can be removed by an after-wash with a sequestering agent to achieve a 'white' resist (Provost, 1988). The dyes that have proved suitable for dyeing ground shades are C.I. Disperse Yellow 50, 83, C.I. Disperse Red 11 (Fig. 10.23), 60, 92 (Fig. 10.24), 184, C.I. Disperse Violet 23, 28 (Fig. 10.25) and C.I. Disperse Blue 26 (Fig. 10.26), 56, 58, 73, 81.



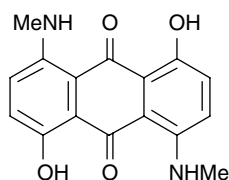
10.23 C.I. Disperse Red 11.



10.24 C.I. Disperse Red 92.



10.25 C.I. Disperse Violet 28.



10.26 C.I. Disperse Blue 26.

Alkali-soluble dyes are also used for the discharge printing of polyester, and the chemistry of these dyes is discussed above under Section 10.2.2. The representative dyes are C.I. Disperse Yellow 126, C.I. Disperse Orange 127, C.I. Disperse Red 278, 311, C.I. Disperse Blue 284, 288, C.I. Disperse Green 9 and C.I. Disperse Brown 19 (Brierley and Provost, 1983).

### 10.3.8 Dyes for polyester-cellulose fibre blends

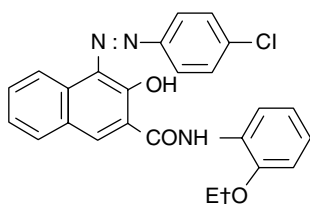
The dyeing of PC fibre blended fabrics is usually carried out by using a two-stage dyeing process to dye the individual fibres, with disperse dyes used for polyester and reactive, vat or direct dyes for the cellulosic component. Printing is generally carried out by a pigment printing process. These dyeing and printing processes are claimed to impart high wet fastness but are time-consuming and therefore expensive to operate.

During the mid-1970s a system based on disperse dyes fixed at high temperature with solvent assistance was developed. In this system the dye

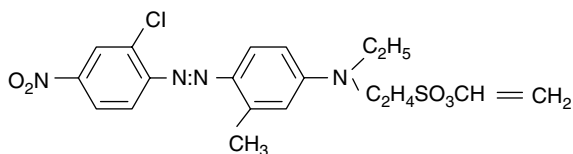
dissolves in the solvent and diffuses not only into polyester but also into the swollen cellulosic phase during fixation. On cooling the dye in the cellulose precipitates and during subsequent washing the solvent is removed, leaving most of the water-insoluble dye behind. The disperse dyes used in this system dissolve in polyethylene glycol (Glyezin CD) at high temperature, give good build-up on both the fibres and are insoluble in Glyezin CD at room temperature. Some of the disperse dyes used in this system are C.I. Disperse Yellow 212, 213, 214, C.I. Disperse Orange 141, C.I. Disperse Red 220 (Fig. 10.27), 321, 322, C.I. Disperse Violet 89, C.I. Disperse Blue 327, 328, 329 and C.I. Disperse Brown 21 (Miksovsky, 1980).

Nishida *et al.* (1974) have reported the use of a one-bath, single-stage process for dyeing PC fibre blended fabrics with disperse-reactive dyes developed from  $\omega$ -chloro-4-aminoacetophenone. Unfortunately, these dyes had low fastness to light. Subsequently, Nishida *et al.* (1974) synthesised monoazo reactive disperse dyes containing a vinylsulphonyl group (such as Fig. 10.28) and investigated their dyeing and suitability for heat-transfer printing properties on PC blends. These dyes were sorbed by polyester as disperse dyes from the dye dispersion in the presence of a carrier and as reactive dyes for cellulosic component under alkaline conditions. The good light fastness exhibited by these dyes has been attributed to the strongly electron-withdrawing vinylsulphonyl group of the dyes.

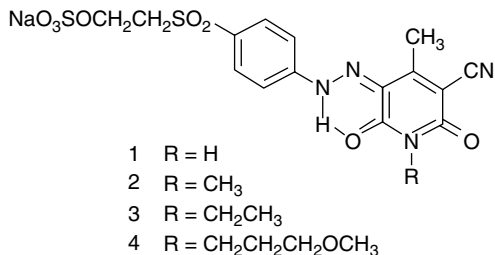
In another study the application of temporarily solubilised reactive disperse dyes on polyester/cotton blends using a one-bath dyeing method has been reported (Lee *et al.*, 2003). In this study, a series of temporarily solubilised reactive disperse dyes based on hydroxypyridone derivatives of sulphatoethylsulphonyl group (Fig. 10.29) were synthesised.



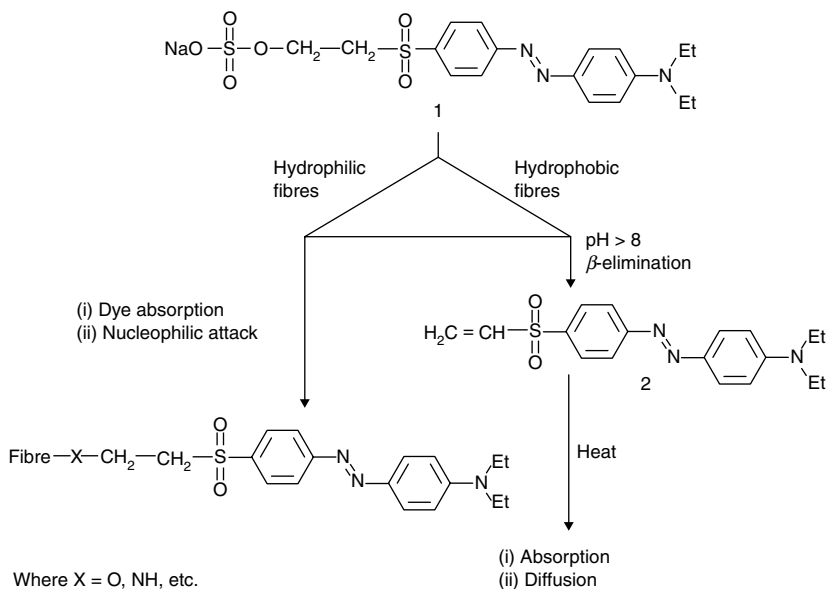
10.27 C.I. Disperse Red 220.



10.28 Vinylsulphone-based disperse dyes.



### 10.29 Hydroxypyridone derivatives containing sulphatoethylsulphonyl group.



### 10.30 Mechanism for application of a vinylsulphone-based dye on hydrophilic and hydrophobic substrates such as PC blends.

These dyes are not only solubilised but also have the ability to react with cellulosic fibres, as the  $\beta$ -sulphatoethylsulphonyl group is converted to a reactive vinyl sulphone group. The elimination of the temporary solubilising group during dyeing produces a non-ionic disperse dye that is sorbed by hydrophobic fibres such as polyester.

Figure 10.30 proposed by Hinks *et al.* (2003) illustrates the mechanism for the application of a vinylsulphone-based disperse dye, 2-[(4-((E)-[4-(diethylamino) phenyl]-diazenyl) phenyl) sulphonyl] ethyl sodium sulphate, on hydrophilic and hydrophobic substrates such as PC blends.

A novel method of dyeing PC blends by a single-stage dyeing process with a combination of disperse and reactive dyes has been proposed by Koh *et al.* (2004). These authors synthesised novel alkali-clearable monoazo disperse dyes based on 4-(N,N-diethylamino)-4'-fluorosulphonylazobenzene and applied them to PC blends along with temperature-stable reactive dyes. The disperse and reactive dyes are added at the start of the dyeing process, which is carried out under acidic conditions at 130°C to fix the disperse dye. The dye bath is then cooled to 80°C and sodium carbonate is added to fix the reactive dye, before washing. It is presumed that during the alkaline phase of dyeing the superficially sorbed disperse dye on polyester and cotton is hydrolysed (see Fig. 10.8) and washed off, yielding good fastness properties on the dyed fabric.

### 10.3.9 Disperse dyes for ink-jet printing

Ink-jet printing is currently one of the fastest growing digital imaging technologies. Although ink-jet printing of textiles at present accounts for <1% of all printed fabrics, this figure is expected to rise to around 10% during the early part of the next decade. One of the factors affecting this growth will be advances in the development of printing inks.

Inks based on disperse dyes that are commercially available are used for the direct printing of polyester fabrics as well as for the printing of paper meant for sublimation transfer printing. Some of the dyes suitable for transfer printing are mentioned in Section 10.3.5. The inks used for sublimation transfer are chemically similar to those used for direct disperse dye printing; the same ink can often be used for both purposes, as is the case with Terasil® TS disperse inks (Huntsman) and Bafixan® P 100 HS (BASF).

According to Fryberg (2005) very few genuinely new developments in dyes specifically designed for textile ink-jet printing have taken place recently. The inks used for this purpose consist of carefully selected dyes taken from the large stock of known dyes. Some suggested dyes include C.I. Disperse Red 86, 88, 92, 126, 135, 145, 152, 159, 177, 181, 206, 283, 348; C.I. Disperse Blue 56, 73, 128, 154, 165, 183, 201, 214, 224, 257, 266, 267, 287, 368 and C.I. Disperse Yellow 56 (Shirota *et al.*, 1999).

A trichromatic combination of yellow, magenta and cyan, along with black dyes, is usually used for the preparation of inks. Black is obtained by blending the other three dyes. The criteria for the selection of the suitable dyes are (a) high material safety, (b) good storage stability and (c) excellent colour fastness of prints (Kawashima *et al.*, 2003). Some of the commercial inks that claim to meet this criteria are Jettex D disperse dye inks (DyStar) and Terasil DI-HL (Huntsman).

## 10.4 Properties of disperse dyes

### 10.4.1 General

Disperse dyes are usually sold as powders, which are prepared by milling the press cake with an equal weight of a suitable auxiliary product and a little water, drying, and then mixing with diluents to give a product containing 15–40% dye. The very fine particle size ( $\leq 1 \mu\text{m}$ ) provides a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate is significantly influenced by the choice of dispersing agent used during the grinding.

These dyes have a bulk density of 0.4–0.6, pH value of 7.0–9.0 (10 g/L water), Chemical Oxygen Demand (COD) of 1.2–1.7 gO<sub>2</sub>/g, BOD<sub>5</sub> of <0.01–0.05 gO<sub>2</sub>/g, LC50 (rainbow trout) (96 h) of >100 mg/L and LD50 of >2000 to >5000 mg/kg.

The general structure of disperse dyes is small, planar and non-ionic, with attached polar functional groups like hydroxyalkyl,  $-\text{NO}_2$  and  $-\text{CN}$ . The shape makes it easier for the dye to slide between the tightly packed polymer chains, and the polar groups improve water solubility and dipolar bonding between dye and polymer, as well as affecting the hue of the dye. The interactions between dye and polymer are thought to be van der Waals and dipole forces.

### 10.4.2 Solubility, particle size, crystallinity and dispersion stability

Initially it was thought that disperse dyes were virtually insoluble in water and that dyeing occurred as a result of the direct transfer of particles to the fibre surface followed by their dissolution inside the fibre. It was later discovered that dyes in aqueous medium dissolve in water and individual molecules diffuse into the fibre during dyeing. There is a dynamic equilibrium between the dye in solution and the dye in dispersion. The solubility of disperse dyes has been attributed to the amino, hydroxyethylamino, azo, carbonyl and other such groups in the dye. These groups have electronegative atoms (nitrogen, oxygen and sometimes sulphur) which can interact strongly with water molecules. Aromatic rings, even if free from such atoms, can also play a part in the interactions of the dye with water molecules and can modify the solubility of the dye (Jones, 1984).

The aqueous solubility of disperse dyes has been extensively investigated and solubility data are available for most of them. In a pioneering study Bird (1954) concluded that aqueous solubility has some bearing on the rate of dyeing of disperse dyes and largely governs their levelling power. The same study also found that the addition of dispersing agents promoted dye solubilisation, particularly above the critical micelle concentration of the



agent. In the initial studies the solubility of the dyes was measured in a temperature range of 25–90°C and was found to be in the range of 5–30 mg/L. In subsequent studies that measured the solubility of dyes in the temperature range of 60–140°C by pressure filtration (Datyner, 1978), the polymer cell method (MPC) (P-ikryl *et al.*, 1979) and titration (Braun, 1991) it has been shown that the solubility varies between 3.3 and 419 mg/L.

In addition to the solubility, the rate of solubilisation of the dye can also influence the dyeing rate for disperse dyes applied to polyester (Odvárka and Hu-ková, 1983). According to Braun (1983) disperse dye particles of  $\leq 1 \mu\text{m}$  form unstable colloidal dispersions that go into solution. Moreover, the solubility of the dye depends on the particle size and degree of crystallinity. The degree of crystallinity of the dye may change during dyeing due to Ostwald ripening and crystal growth (Chung *et al.*, 2001).

The particle size of disperse dyes is an important parameter influencing the dyeing behaviour of the dye. Many studies have investigated the effect of disperse dye particle size on dyeing properties. In addition, the crystalline properties of disperse dyes differ from one another, and different crystal forms show different dispersion behaviour (Leube, 1978). Many reports have demonstrated the effect of the crystalline properties of the dye on the dyeing performance of disperse dyes (Apperley, 1969; Biedermann, 1971; Shenai and Sadhu, 1976). The particle size and crystallinity of the dye can be reduced by ultrasound irradiation, has a more significant effect on the breakage of well-crystallised dye particles than on poorly crystallised dye particles (Lee *et al.* 2001).

Surface active agents incorporated during production as well as introduced into the dyebath increase the solubility and stability of the dispersion. It is postulated that the surface active agents are sorbed on the surface of the dye particle, impart negative charge to the dye. The temporarily negative charge on the dye particles results in the repulsion of the particles, thus contributing to their stability. Moreover, as stated above, disperse dyes are solubilised in the micelles of the surface active agents. Hence the dye dispersion contains dye solubilised in water and dye solubilised in the micelles. Consequently, during the dyeing process the dye may be distributed between the aqueous phase and the pseudo-phase consisting of the micelle core and surface. The mechanism by which dye is released from this pseudo-phase to affect sorption by the fibre is not known (Jones, 1984).

## 10.5 Future trends

### 10.5.1 Dispersant-free disperse dyes

Dispersing agents present in the commercial dyes keep the dyes in fine dispersions in the dyebath. An additional dispersing agent is added to the

dyebath to increase the dispersion stability, solubility, levelling and fastness properties of the dyes. During dyeing, dispersing agents can have a reducing effect on the dye and after dyeing they add to the COD and BOD of the effluent. To counteract some of these environmental concerns, DyStar has recently introduced a range of 'Green' disperse dyes having ecofriendly chemicals under its econfidence® programme.

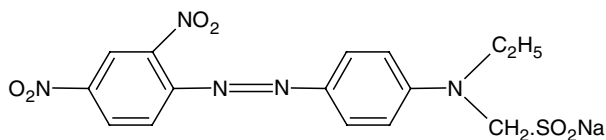
The problem caused by the use of dispersing agents is gradually being resolved through the development of disperse dyes containing temporarily solubilising groups. Another means of avoiding the use of dispersing agents is dyeing with microencapsulated dyes.

#### *Disperse dyes containing temporarily solubilising groups*

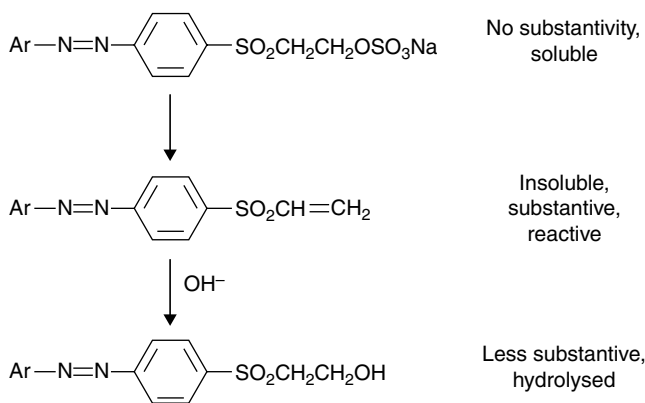
Ionamines (Fig. 10.31) were the first temporarily solubilised disperse dyes synthesised by Green and Saunders in 1923. These dyes are hydrolysed in the dyebath during dyeing to form insoluble species that are adsorbed onto the surface of the fibre, and diffuse into it. These dyes can be dyed without the use of dispersing agents.

However, the rate of hydrolysis was not the same for all dyes of this type, leading to problems in shade matching. Moreover the colours of the final dyeings were also different from those of the original dye solutions, owing to the hypsochromic effect associated with the loss of the alkyl group that carries the solubilising group. The diffusion of ionamine dyes was recently studied by Guo (2005).

In another approach, disperse dyes based on temporarily solubilising  $\beta$ -sulphatoethyl-sulphonyl groups have been successfully applied on polyester without the use of a dispersing agent. Although Dohmyou *et al.* (1990) were the first to apply these dyes for the simultaneous dyeing of silk and synthetic fibres, a detailed investigation into the hydrolysis of these dyes was not conducted until Lee and Kim (1999a). Depending on the pH and temperature conditions in the dyebath, soluble dye molecules are gradually converted through  $\beta$ -elimination (Fig. 10.32) to insoluble derivatives that have an affinity to polyester. According to these investigators the optimum pH, which gave moderate hydrolysis rates for dispersant-free polyester dyeing, was between pH 5.0 and 6.0.



10.31 Ionamines.



10.32  $\beta$ -elimination for conversion of soluble dye molecules.

In a subsequent paper the same authors reported (Lee and Kim, 1999b) that at pH 5.0 the rate of hydrolysis of the dye was moderate, which allowed temporarily solubilised disperse dyes to be successfully applied to polyester without the use of dispersants.

#### *Microencapsulated disperse dyes*

The technique of microencapsulation of dyes was developed during the early 1970s, and a range of microencapsulated dyes was produced for printing of polyester fabrics to achieve a 'speckled' effect (Hiroshi and Tsugio, 1973). Subsequent studies have shown that the capsule wall acts as 'a very low diffusion barrier'. For the diffusion from the microcapsules,  $\Delta E$  (activation energy) is a little larger than that from a free state (Sawanoi *et al.*, 2000). Many studies on transfer printing and control lease of these dyes on polyester substrates have been carried out by Yan *et al.* (Yan and Shuilin, 2001, 2003; Yan *et al.*, 2002) of the College of Chemistry and Chemical Engineering, Dong Hua University, Shanghai.

A significant study carried out at this university (Yi *et al.*, 2005) indicates that the polyurea microcapsules of disperse dye in the core and diphenylmethane-4,4'-diisocyanate as the wall-former (shell) could be dyed on to polyester by a high temperature dyeing process without dispersing agents, penetrating agents, levelling agents or other auxiliaries. The quality of the polyester fabric dyed in this manner – without reduction clearing – was as good as that dyed traditionally after washing and reduction clearing. After separating off the polyurea microcapsules, the dyebath was virtually colourless and was shown to be suitable for reuse. The possibility of recycling microencapsulated disperse dyebath effluents has been further explored by Ji *et al.* (2009). According to this study, the effluent can be reused several

times after being simply filtered and can be used as a solvent for PET fabric scouring.

In a recent similar study Zandi *et al.* (2010) created a nano film through layer by layer deposition of weak polycation poly(allylamine hydrochloride) and strong polyanion poly(sodium styrene sulphonate) on the surface of disperse dye particles. These particles were then enclosed in poly(urea formaldehyde) by *in situ* polymerisation. On dyeing, these microcapsules slowly release the dye and do not require the use of any auxiliary chemicals.

### 10.5.2 Stimuli-sensitive dyes

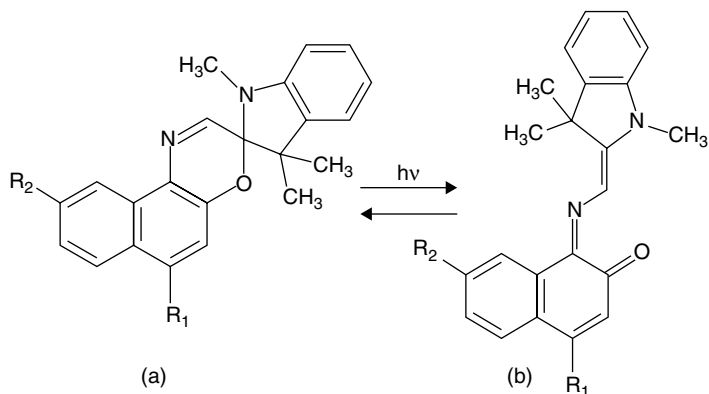
Stimuli-sensitive colourants are increasingly being used in the production of smart textiles. The applications of colour-changing dyes on textile materials are being exploited for functional effects such as camouflage, security printing and brand protection and for use in 'smart' textile applications in general.

A coloured textile material may respond if there is excessive stress on it; alternatively there may be a change in colour or the appearance of colour at a particular temperature (thermochromism) or under a particular illumination (photochromism). Many textiles displaying thermochromic and photochromic properties have been developed, and the application of these photochromic colourants on polyester has also been recently investigated.

#### *Photochromic disperse dyes*

The phenomenon of photochromism, i.e. the reversible change from a colourless to a coloured form of a compound when exposed to UV or visible light, was discovered in the 1880s and was commercially exploited in the production of photochromic ophthalmic lenses by Corning (USA) in 1966. A recent comprehensive review by Corns *et al.* (2009) describes how photochromism has been commercially exploited, placing emphasis on the chemistries of the colourants that are industrially important, namely spiropyrans, spirooxazines and naphthopyrans (also known as chromenes).

Billah *et al.* (2008) have studied the dyeing of polyester with spirooxazines. Spirooxazines are colourless latent dyes that (1) on exposure to UV light, turn into coloured dyes by ring opening and (2) revert thermally to the ring-closed form when the light source is removed (Fig. 10.33). This study has demonstrated that substituted spirooxazines (Fig. 10.33a and b) are sorbed by polyester as disperse dyes. The dyes are mostly sorbed on the periphery of the fibre and have good wash fastness.



10.33 Spirooxazines showing (a) ring opening on exposure to UV light; (b) thermal reversion to ring-closed form on removal of light source.

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**Abstract:** Dyes have been extracted from natural resources since ancient times: the use of natural colourants poses no problems in terms of waste disposal and can provide a natural finish to textiles. The chapter first discusses the classification and chemistry of natural dyes, and then describes the ways in which they can be applied to textiles, relying on modern scientific advances to reintroduce biodegradable and environmentally friendly natural dyes.

**Key words:** chemistry, dyeing, eco-friendly, mordant, natural dyes, textiles.

## 11.1 Introduction

The practice of applying colour through dyeing and printing techniques has played a significant role in every civilisation. Egyptian mummies and documents from the Mughal periods in India bear witness to the early utilisation of natural dyes (Ramakrishna, 1999). In 1856, William Henry Perkin synthesised a basic dye, Mauveine, by chance. With the advent of coal tar dyes (now synthetic dyes), there was a substantial decrease in the use of natural dyes, because those currently available did not fulfil the increasingly high demands of the consumer market (Smith and Wagner, 1991).

However, many synthetic dyes, particularly azo dyes which are prepared from -arylamines, have been found to be potentially carcinogenic. Certain chemicals used in the synthesis of dyestuffs are also regarded to be carcinogenic or mutagenic as well as sensitising or allergenic (Gulrajani, 1992). Thus, based on the EC Control of Substances Hazardous to Health Act, 1989, a number of chemicals have been banned in the USA and Europe. As a result, less hazardous, eco-friendly natural dyes have enjoyed a renaissance, and are particularly widely used by a number of textile manufacturers (including handloom manufacturers) (Glover and Pierce, 1993).

### 11.1.1 Strengths and limitations

Natural colourants are unsophisticated and harmonised with nature. They are obtained from renewable sources and their preparation involves very little

potential for chemical reactions (Dalby, 1993). Hence, they are not hazardous to health, and can sometimes even have a curative effect. Furthermore, the use of natural dyes does not pose any problems with regard to disposal of the product (Sewekow and Bayer, 1995). However, not all natural dyes are eco-friendly. Heavy metals or other potentially toxic substances may be present in some natural dyes (Joshi and Purwar, 2004). Natural dyes must therefore also be tested for toxicity before use. Generally, natural dyes have the following limitations.

- Limited number of suitable dyes, leading to a similarly limited range of shades.
- Colour yield and efficiency both of dyeing and of cultivation.
- Reproducibility of shades.
- Process complexity.
- Availability: natural resources are not available in all countries.

Apart from these limitations, there are various other technical drawbacks also associated with the use of natural dyes (Schweppe, 1992). These are as follows:

- Limitations on fabric that can be dyed (mostly only wool, natural silk, linen and cotton).
- Low suitability for synthetic fibres.
- Difficulties in blending dyes to produce compound shades (Samanta *et al.*, 2008).
- Lack of standardisation.
- Difficulty in collecting the dyes.
- Inadequate degree of fixation and fastness properties.
- Water pollution caused by heavy metals used for mordanting specific dyes, which remain unfixed in the dyebath effluent (Chavan, 1995).

Despite the numerous limitations associated with the use of natural dyes they still have the potential to change wet processing of textiles, thanks to their eco-friendly nature, the lack of hazardous chemicals needed for synthesis, and several other advantages.

## 11.2 Classification of natural dyes

Natural dyes can be defined as those colourants (dyes and pigments) obtained from animal or vegetable matter with no processing involved. For textile dyeing, the most commonly used are mordant dyes, although some belong to other groups (vat, solvent, pigment, direct and acid). Most of the historically important colourants are members of the anthraquinone, naphthoquinone, indigoid and carotenoid groups. There are no natural dyes of the sulphur, disperse, azoic or ingrain types.

Natural dyes can be classified in various ways (Agarwal and Patel, 2000). Early methods of classification were based simply on the alphabetical arrangement of dyes. Later on, numerous other methods of classification were adopted, which are as follows:

- Classification based on chemical structure
- Classification based on their origin or the sources from which they are obtained
- Classification based on their methods of application
- Classification based on their colour.

In the Colour Index, natural dyes are arranged and classified according to their chemical composition as well as their major applications (Glower, 1998). Natural dyes make up a separate section in the Colour Index, where they are arranged according to hue within their application category.

### 11.2.1 Classification based on chemical structure

Natural organic dyes and pigments belong to a wide range of chemical classes, such as indigoid, anthraquinonoids, naphthoquinones, polymethines, ketones, imines, quinones, flavones, flavanols, flavanones and chlorophyll. Some of the important chemical classes are represented in Table 11.1.

### 11.2.2 Classification according to source

Depending on their origin or the sources from which they are produced, natural dyes can be grouped into three distinct classes: those derived from vegetable sources; those derived from insect or other animal sources and those derived from mineral sources.

#### *Dyes derived from vegetable sources*

Vegetable dyes are obtained from various parts of plants and herbs including the stem, wood, roots, bark, leaves, flowers, fruits and skin of plants, which produce distinct pale to dark shades on both natural as well as synthetic fibres. Some important examples of dyes derived from plants or vegetables are logwood, turmeric, pine wood, catechu, madder, etc.

#### *Dyes derived from insects or animal sources*

Some of the most important red dyes, based on the anthraquinone structure, are obtained from insects or animals. These dyes are characterised by good light fastness. They combine with metal salts to form metal-complex dyes, which possess good wash fastness. Examples of this type of dye are Lac, Kermes, Cochineal, Lichen, etc.

Table 11.1 Important chemical classes of natural dyes

Chemical class	Natural dye source	Substrate	Colour produced
Indigoids	Indigo ( <i>Indigofera tinctoria</i> )	Cotton, wool and silk	Blue
	Woad ( <i>Isatis tinctoria</i> )	Cotton, wool and silk	Blue
	Tyrian purple ( <i>Purpurohaemastroma/Murex brandaris</i> )	Cotton, wool and silk	Blue purple/reddish purple
Anthraquinonoids	Madder ( <i>Rubia tinctorium</i> )	Wool and silk	Pink, red crimson orange, brown and maroon*
	Manjith ( <i>Rubia cordifolia</i> )	Wool and silk	Pink, red crimson orange, brown and crimson*
	Lac ( <i>Laccifer lacca</i> )	Wool silk and nylon	Red, scarlet, crimson and brown*
	Kermes ( <i>Kermes vermilio</i> ) Cochineal ( <i>Coccus cacti</i> )	Wool Wool, silk and cotton (printing)	Red and purple* Crimson, scarlet and pink*
Alphanaphthaquinones	Heena or lawsonne (leaves of <i>Lawsonia inermis</i> )	Wool and silk	Yellow to brown
	Juglone (shells of <i>Juglans regia</i> ) Weld ( <i>Reseda luteola</i> )	Wool and silk Cotton, wool and silk	Brown Yellow, orange and olive
Flavones Dihydroxytrons	Logwood (compeachy wood, <i>Haematoxylum campechianum</i> )	Wool, silk, cotton and leather	Black
	Brazilwood (red wood species, <i>Caesalpinia echinata</i> )	Wool, silk and cotton	Crimson, black and purple*
	Sappanwood (red wood species, <i>Caesalpinia sappan</i> )	Wool, silk and cotton	Crimson, black and purple*
Anthocyanidins	Carajurin (leaves of <i>Bignonia chica</i> ) Awobanin (clowers of <i>Tsuyukusa cammelia communis</i> )	Cotton and silk Silk	Orange Blue
	Annatto ( <i>Bixa orellana</i> ) Saffron ( <i>Crocus sativus</i> )	Wool and silk Wool and silk	Yellow and orange Yellow

\*Indicate different colours with different mordant.

### *Dyes derived from mineral sources*

Natural dyes produced from mineral resources include chrome yellow, chrome orange, chrome green, iron buff, Prussian blue, manganese brown, mineral khaki, etc. Mineral colours are not dyes but inorganic compounds, insoluble in water and precipitated onto the fibre by double decomposition. Certain important minerals widely used as natural dyes are Cinebor (Sangraj), Red Lead (Sindur), Laminated Red earth (Gem), Ultramarine (Lajerd), Zinc white (Sajeda), etc.

### 11.2.3 Classification according to method of application

According to this classification, natural dyes can be classified as either direct dyes or mordant dyes (Sekar, 1999). Direct dyes may be further subdivided into:

- Direct dyes for cotton, e.g. turmeric, pomegranate, annatto, safflower, etc.
- Direct dyes for wool and silk, e.g. turmeric, pomegranate, annatto, safflower, etc.
- Acid dyes, e.g. saffron
- Basic dyes, e.g. Berberine.

Direct dyes for cotton can be applied to all natural textile fibres; acid dyes can generally only be applied to wool and silk; basic dyes can be used for wool and silk as well as tannic acid treated cotton. On the other hand, mordant dyes are equally suitable for both animal and vegetable fibres. Important mordant dyes include madder, logwood and cochineal. There is a further class of dyes known as vat dyes, which are insoluble in water. These include indigo, woad and tyrian purple.

### 11.2.4 Classification based on colour

Natural dyes are frequently categorised on the basis of the colour that they impart to the fibre substrate (Paul *et al.*, 1996).

#### *Natural yellow dyes*

Yellow symbolises growth and happiness and is perhaps the most abundant hue in nature. The number of plants that yield yellow dyes is much higher than the number that yield other colours, and the Colour Index lists a total of 28 natural yellow dyes. Yellow is of particular significance in India, where it is still considered an auspicious colour with great religious significance. Some of the yellow dyes which have been most commonly used are shown in Table 11.2.

Table 11.2 Natural yellow dyes

Class of dyes	Common name	Botanical name
Flavanoid dyes	French marigold	<i>Tagetes patula</i> , <i>Tagetes erecta</i>
	Flame of the forest	<i>Butea monosperma</i> , <i>Buteafrondosa</i>
	Jackfruit	<i>Artocarpus heterophyllus</i> , <i>integrifolia</i>
	Kamala	<i>Mallotus philippinensis</i>
Carotenoid dyes	Kaiphal	<i>Myrica esculenta</i>
	Onion	<i>Allium cepa</i>
	Yellow larkspur	<i>Delphinium zailii</i>
	Annatto	<i>Bixa orellana</i>
	Saffron	<i>Crocus sativus</i>
	Harsinghar	<i>Nyctanthes arbortristis</i>
Diaroyl methane dyes	Indian mahogany	<i>Cedrela toona</i>
	Turmeric	<i>Curcuma tinctoria</i> , <i>Curcuma longa</i>
	Barberry	<i>Berberis aristata</i> , <i>Berberis vulgaris</i>
Quinonoid dyes	Dolu (Himalayan rhubarb)	<i>Rheum emodi</i>
	Heena	<i>Lawsonia inermis</i>

Colour Index lists 28 yellow natural dyes.

Table 11.3 Important natural red dyes

Natural source	Common name	Botanical/zoological name
Plant sources	Saffron	<i>Carthamus tinctorius</i>
	Madder	Indian madder ( <i>Chay</i> ; <i>Oldenlandia umbellata</i> ), English madder ( <i>Rubia tinctorium</i> )
Animal sources	Patang	<i>Caesalpinia sappan</i>
	Lac	<i>Laccifer lacca</i>
	Cochineal	<i>Coccus cacti</i>
Mineral sources	Kermes	<i>Kermes vermilio</i>
	Geru	Laminated red earth
	Sulphide of mercury	Cinnabart

### Natural red dyes

The Colour Index lists 32 natural red dyes: some are extracted from the roots or bark of plants, while others, such as cochineal, are camouflaged in the bodies dull grey insects. However, the sources of these dyes are limited. Throughout history, natural red dyes have been of significant – and in some cases legendary – importance. Almost all natural red dyes have a basic quinone structure. They are mainly comprised of anthraquinones

(alizarin, purpurin, munjistin, laccaic, etc.) or naphthoquinones (alkannin and shikonin); there is also one benzoquinone dye (carthamin). Some of the prominent natural red dyes, as obtained from plant, animal (*Erica et al.*, 1995) and mineral sources (Mohanty *et al.*, 1987) are listed in Table 11.3.

### Natural blue dyes

The Colour Index lists only three natural blue dyes, namely natural indigo, sulphated natural indigo and the flowers of the Japanese *Tsuyukusa*, used mainly for paper making. The most brilliant and the fastest blue shades are obtained from indigo on all fibres. The principal colouring matter is indigotin, whose main sources are Indigo (*Indigofera tinctoria*) and woad (*Isatis tinctoria*).

### Natural black dyes

One important black natural dye is Logwood (*Haematoxylum campechianum*) which is also known as Cam peachy wood because it was discovered by the Spaniards on the bay of Campeche in Mexico. It is still used today for dyeing silk in deep shades on an iron tannate mordant. It also gives excellent depth and fastness on most natural and synthetic fibres (Knecht *et al.*, 1933). Tannins are further important sources of black dyes. Pomegranate rind contains the hydrolysable tannic flavogallol, which combines with iron salts to give deep blacks.

### Natural brown dyes

The majority of natural brown dyes are obtained from quinone-based dyes, naphthoquinones and anthraquinones. Generally, copper and iron salts are used as mordants and they tend to turn the colour to dull and deep shades, particularly browns. Table 11.4 presents some widely used natural brown colours. In addition to those mentioned in Table 11.4, there is one other natural dye, cutch, which produces rich brown shades with copper and chromium salts. This dye is a tannin-based flavonoid, and is derived from *Acacia catechu* and wild *Acacia arabica* (Forrester, 1975).

Table 11.4 Important natural brown colours

Class of dyes	Common name	Botanical/zoological name
Naphthoquinones	Sanderswood	<i>Pterocarpus santalinus</i>
	Anthraquinones	<i>Coccus cacti</i>
	Chayroot	<i>Oldenlandia umbellata</i>
	Manjith	<i>Rubio cordifolia</i>
	Madder	<i>Rubia tinctorium</i>
	Lac	<i>Luccifer lacca</i>
	Dolu	<i>Rheum emodi</i>

### 11.3 Chemistry of natural dyes

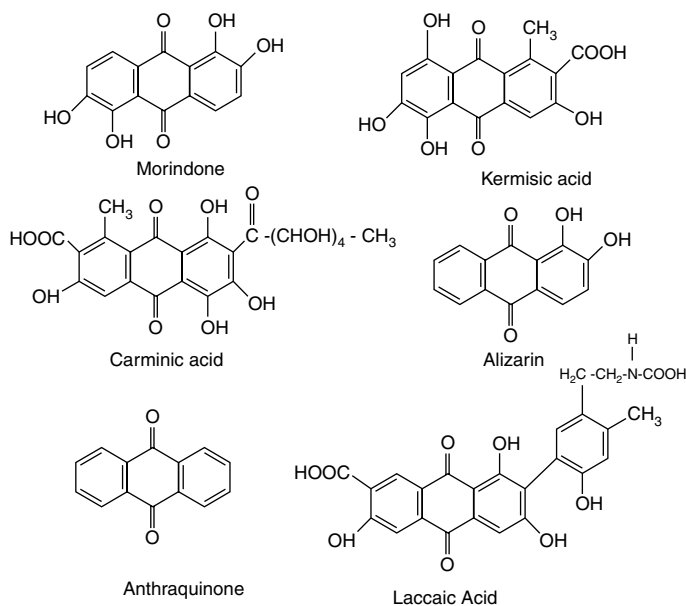
In plants the coloured pigments are normally present in the leaves, flowers, heart wood, bark and roots. These pigments can be extracted from the plant parts using suitable solvents depending on the chemical nature of the coloured constituents. The major divisions of natural chromogens that are or could be used in food materials and pharmaceuticals are listed below, along with examples of pigments and sources (Mayer and Cook, 1943).

#### 11.3.1 Anthracenes

The two major groups of the anthracenes contain several well-known dyes.

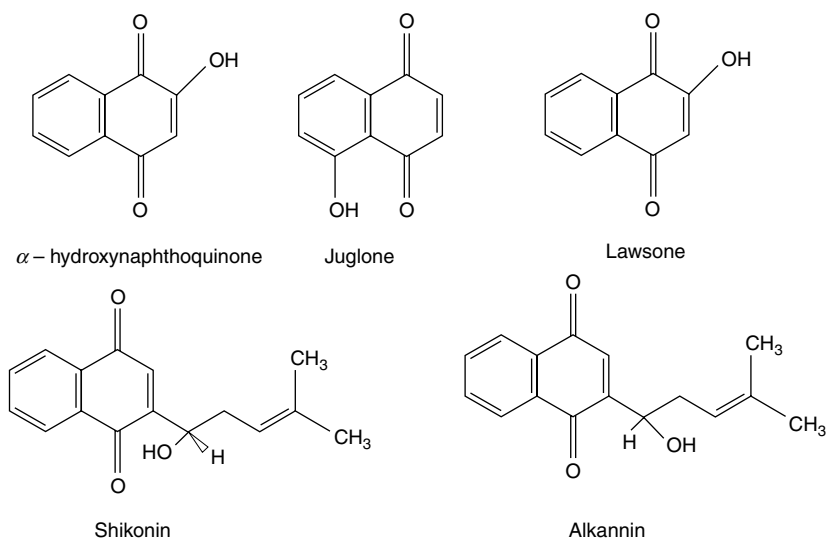
Anthraquinones (yellow, pink and red pigments) (Saidman *et al.*, 2002) include *Morinda citrifolia* (Morindone), *Alkanna tinctoria*, *Dactylopius coccus* (cochineal) (carminic acid), *Laccifer lacca* (Lac insect) (Laccaic acid), *Kermes ilicis* (shield louse) (Kermisic acid), *Alnus glutinosa*, *Rubia cordifolia*, *Rubia tinctoria*, etc. (Alizarin) (Ruberethric acid). The structures of some anthraquinone dyes are shown in Fig. 11.1.

Naphthoquinones (brown, pink or purple pigments) include *Juglans nigra*, *Juglans regia* (Juglone), *Lawsonia innermis* (Lawsonie), *Woodfordia fruticosa*, *Lawsonia alba* (Lawsonie), *A. tinctoria* (Alkannin) and *Lithospermum erythorhizon* (Shikonin). Natural chromogens of these dyes are shown in Fig. 11.2 (Gulrajani *et al.*, 1992c).



11.1 Structures of anthraquinone dyes.





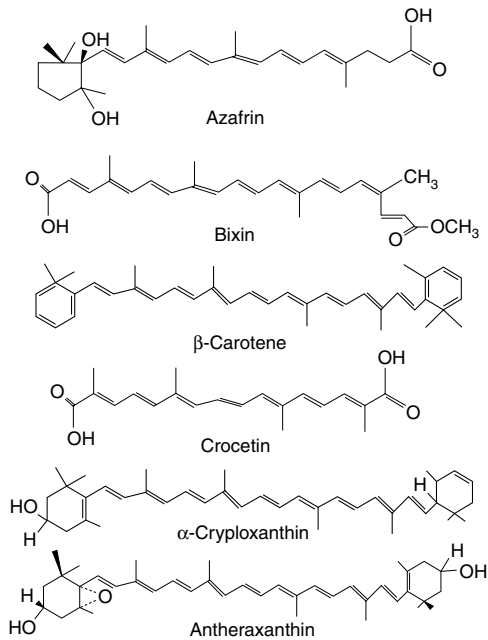
11.2 Structures of some naphthoquinone dyes.

### 11.3.2 Carotenoids (orange, yellow, pink and brown colour pigments)

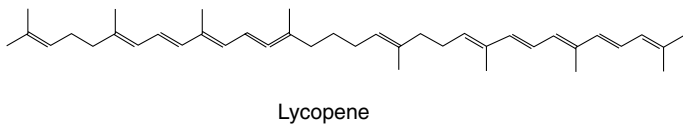
These are a family of yellow and orange pigments found in most photosynthesising organisms. Over 200 naturally occurring carotenoids have been identified but only a few are commercially available, including  $\beta$ -carotene,  $\beta$ -apo-8'-carotenal and canthaxanthin. The two major groups in the family are the carotenes (orange or red-orange) and the xanthophylls (yellow).  $\beta$ -carotene is the major carotenoid in algae and higher plants. Examples of carotenoids are *Christisonia bicolor* (Azafrin), *Careca papaya* fruits (anthera xanthin), *Bixa orellana* (Bixin), *Ziziphus jujube*, *Crocus sativus* (Crocetin), *Rubus fruticosus*, *Daccus carrota*, *Lillium hamsonii* ( $\beta$ -carotene), Zeamays seeds, *Helenium autumnale* (cryptoxanthin), *Ananas comosus*, *Lycopersicon esculatum* and *Rhodo pseudomonas* bacteria. Chemical structures of these colourants are given in Fig. 11.3.

### 11.3.3 Carotenes

Carotene was first isolated as red crystals from carrots in 1831. It is closely related to vitamin A and generally occurs as a mixture of  $\alpha$ -, - and  $\gamma$ -carotene in the ratio 15:85:0.1. Lycopene is the main colourant of tomatoes and is shown in Fig. 11.4.



11.3 Structures of some carotenoid dyes.



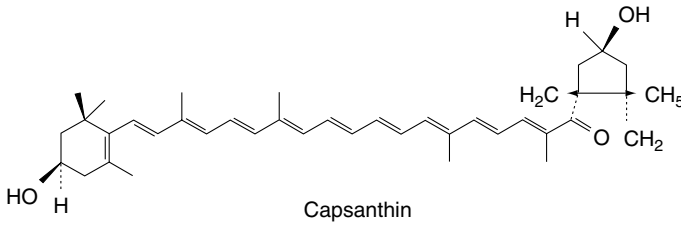
11.4 Structure of Lycopene.

### 11.3.4 Xanthophylls (yellow and red pigments)

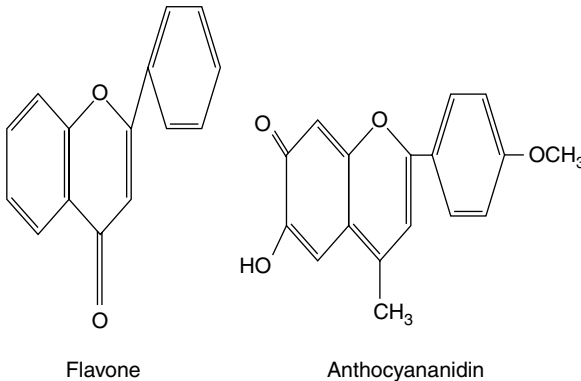
These are oxygenated carotenes. Examples are *Tagetes patula*, *Capsicum annum* (red pigment) (Capsanthin) (see Fig. 11.5), lutein (nettles, French marigolds), cis-bixin (annatto) and crocin (saffron) (Padma, 2000). Annatto is used mainly for colouring dairy products and is derived from *B. orellana*. Saffron (*C. sativus*) (Tsatsaroni and Eleftheriadis, 1994), whose main dye constituent is crocin, is a major colouring agent in use since Ancient Greece and Rome.

### 11.3.5 Flavonoids or flavones (yellow to brown pigments)

Flavonoids are derivatives of phenylalanine and the acetate coenzyme A esters, and are based on a C6-C3-C6 structure (Guinot *et al.*, 2006). The C3



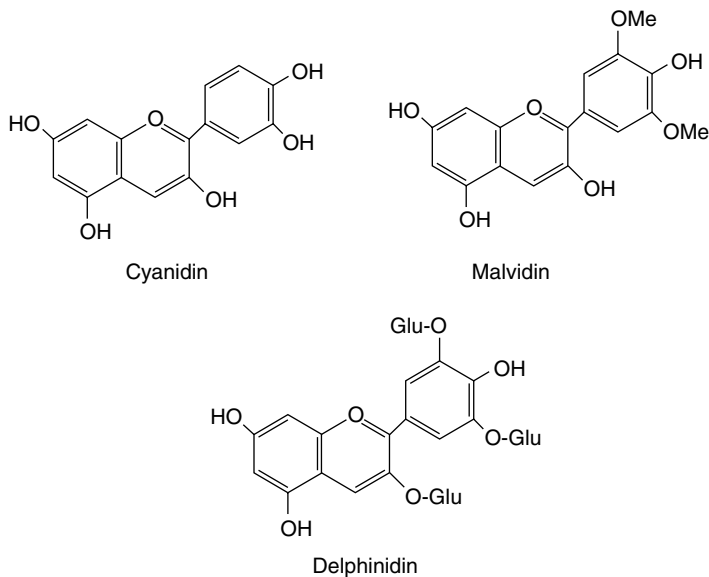
11.5 Structure of capsanthin.



11.6 Structure of flavone and anthocyanidin.

link forms a heterocyclic pyrone ring. The oxidation state of this ring and the hydroxylation or methoxylation of a ring (first C6 group) distinguish the various groups of flavonoids. The three major groups are the flavones, flavonols and anthocyanidins (see Fig. 11.6) (Gulrajani *et al.*, 1992b); others include the anthocyanins, isoflavonoids, chalcones and aurones. Some examples of flavonoids are *Convallaria magalis*, *Butea monosperma*, *Nymphaea alba*, *Madhuca indica*, *Ligustrum vulgare*, *Eupatorium gracile* and weld (*Reseda luteola* L) (Cristea *et al.*, 2003).

Anthocyanidins and anthocyanins (blue, bluish red, mauve, brown, orange and reddish brown pigments) are the most highly coloured of the flavonoids. Twelve anthocyanidins are known. The degree of colour they show is determined by the degree of hydroxylation or methoxylation of the B ring (the second C6 group): specifically, hydroxylation tends to increase blueness, while methoxylation increases redness. Anthocyanins are the glycosides of anthocyanidins, produced by the substitution of sugars for a hydroxyl group. Light, nutrient stress and low temperature stimulate their production, and they are found in plants much more commonly than their parent anthocyanidins. Colourant performance can be modified by the presence of metals, by pH and by interaction with colourless flavonoids. Glycosides of cyanidin

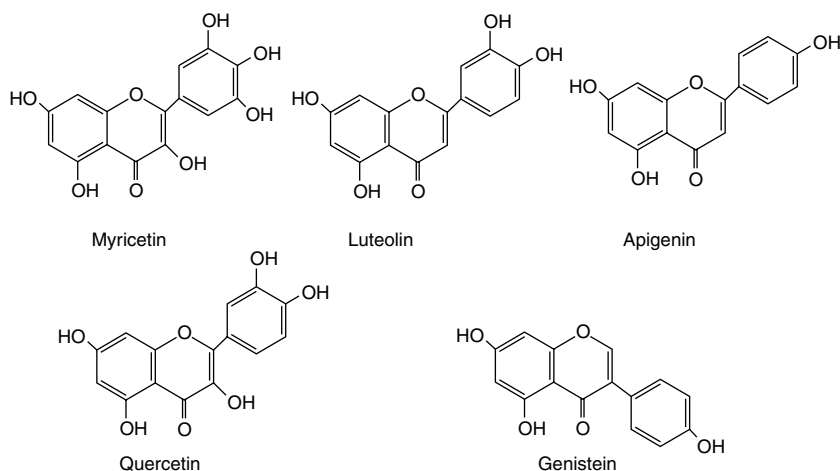


11.7 Structures of cyanidin, malvidin and delphinidin.

are found in more than 80% of pigmented leaves and 50% of flowers. The most frequently occurring glycosides are those of cyanidin, delphinidin and pelargonidin. The most common anthocyanidins are cyanidin (red-purple), delphinidin (blue-purple), malvidin (deep purple), peonidin (red), petunidin (purple) and pelargonidin (orange-red).

Anthocyanins are water soluble and are easily extracted into a weakly acidic solution. This ease of extraction accounts for their widespread early use as dyes and colourants. However, anthocyanidins and anthocyanins are both sensitive to pH, which can restrict their use as colourants in certain situations such as in foods. Some examples are malvidin (mallows), cyanidin (see Fig. 11.7), carajurin (*Bignonia chica*), awobanin (*Commelina communis*), dracorhodin and dracorubin, also known as Dragon's Blood (Natural Red 31) (*Doemonorops propingus*). The last of these has been used in the printing trade for preparing halftone plates for multicolour printing. The food dyes peonidin, from cranberries, and enocionia, derived from grape skins, are both anthocyanidins.

Of the flavonols and flavones (yellows), flavonols tend to fade in strong light, while flavones tend to be more permanent but paler in colour. Examples of these are quercetin, kaempferol and myricetin (many families) fisetin (fustic, nettles, etc.), morin (fustic, Osage-orange, etc.), apigenin (daisy family), luteolin (daisy, pea and weld) and flavone (primrose). Most natural yellows occur in the plant as glycosides or esters of tannic acid. Luteolin was an



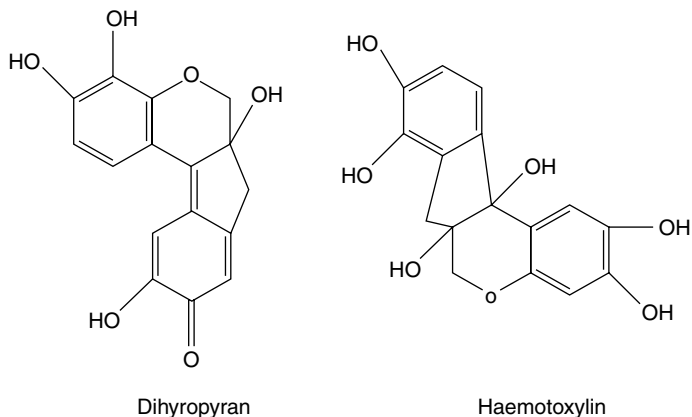
11.8 Chemical structures of some flavonol and isoflavone dyes.

important yellow dye, particularly for the dyeing of gold braid, and weld was cultivated for this purpose in much of Northern Europe. With the appropriate mordant (alum) on silk it is the most light-fast natural yellow dye, and is reported still to be in use in parts of Europe for dyeing leather. Morin can be used on leather, silk and wool, and on nylon when mordanted with chrome. The major source of quercetin is the inner bark of the quercitron tree (*Quercus tinctoria*) but it is also present in horse chestnuts, onion skins, tea and sumac, and in several other plants (Gulrajani *et al.*, 1992a).

Minor flavonoids include: chalcones – coreopsidoside and mareoside (daisy family); aurones – sulphuroside (fustic, daisy family) and isoflavones, which tend to produce strong, permanent colours, such as genistein (pea family) (see Fig. 11.8), osajin and pomiferin (Osage-orange (*Maclura pomifera*)).

### 11.3.6 Betacyanins (betalains)/nitrogen-containing glucosides (red pigment) (oxyindol glycosides)

These red dyes, along with the related betaxanthins (yellows) were originally thought to be flavonoids; however, they differ in that they contain nitrogen and do not undergo the same reversible colour change as anthocyanins when exposed to different pH levels. They are glycosylated, like anthocyanins. They are reported to be present only in a few families of the Chenopodiaceae, such as the beet, portulacca and goosefoot families. Betanin is an extract from the red beet (*Beta vulgaris*), containing red and yellow pigments, which is used mainly as a food colouring. Betanin is the major component (95%) of the red pigments in the extract.



11.9 Chemical structures of dihydropyrans and haematoxylin.

### 11.3.7 Flavins

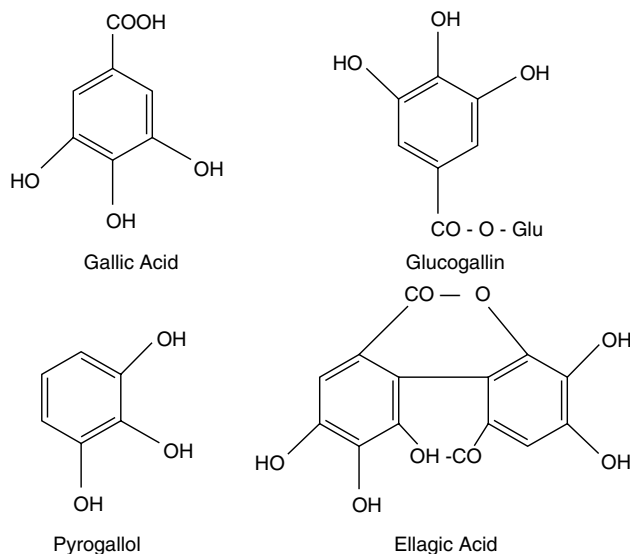
Flavins are very common in living organisms, riboflavin and two of its derivatives being the three most common. Their precise physiological role in the plant is unknown but it is thought that they may be involved as receptors of blue light and UV-A (the receptors for UV-B are unknown). Riboflavin (an alloxan adduct) is a yellow dye closely related to vitamin B2, used for colouring food. This colourant can be synthesised.

### 11.3.8 Dihydropyrans/phenolic derivatives (red, pink and brown pigments)

These are closely related to flavones. The most important dyes are haematin and haematoxylin (see Fig. 11.9), which are the principal colourants found in logwood (*Haematoxylum campechianum*), used traditionally in Mexico and Central America to dye textiles blue. Logwood is used in the leather industry for tanning and dyeing, and was historically the principal source of dark colours on a wide range of natural fibres. The other dyes of significance in this group are *Chlorfora tinctoria* (Maclurin), brazilin and brazilin, from the genus *Caesalpinia*, which produce a red which is vivid but fades quickly.

### 11.3.9 Tannis (reddish brown, black, yellowish brown and bluish black pigments)

Dyes containing tannins are obtained from *Areca catechu*, *Acacia glutinosa*, *Acacia catechu*, *Acacia Arabica* wild, *Pterocarpousmarsupinm*, *Terminalia*

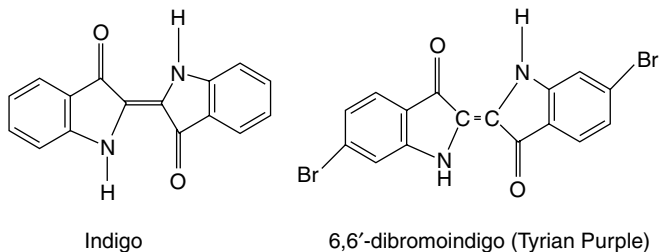


11.10 Structures of tannins.

*chebula*, *Quercus sativa* (Galls) *Prunus persica*, *Embellica officinalis*, *Annona reticulata* and *Amaranthus hypocondriacum*. Tannins are present in most plant tissues but are especially associated with damaged tissues and with bark (Patel and Agarwal, 2000). They are produced from flavonoids, especially anthocyanins, when tissues break down. Hydrolysed tannins (yellowish colours) include gallotannins (see Fig. 11.10) (fustic and oak) and ellagitannins (e.g. sumac, water-lilies). Condensed tannins (reddish colours) are derived from, for example, oak, willow bark, cutch and water-lilies.

### 11.3.10 Indigoid dyes (blue pigments)

Examples of natural dyes containing indigoid are *Indigofera tinctoria* (Koren, 1994), *Wrightia tinctoria* and *Murex brandaris* (shellfish). The two most important dyes in this group are Tyrian purple (see Fig. 11.11), derived from the molluscs *Murex trunculus*, *M. brandaris* and *Purpura lapillus*, and Indigo (see Fig. 11.11). The main dye chemical in tyrian purple is 6,6'-dibromoindigo; the natural source is no longer used because of the large number of shellfish needed to produce even a small amount of the dye and because of the relative rarity of the shellfish. Indigo is known to be present in a small number of plants: indigo (*Indigofera* spp.), woad (*Isatis tinctoria* and other species), a Japanese knotweed (*Polygonum tinctorium*) and common knotweed (*P. aviculare*), *Nerium tinctorium*, *Marsdenia* and *Lonchocarpus cyanescens*. These plants contain the glucoside indican or isatan B, which is soluble in water and



11.11 Chemical structure of indigo and tyrian purple.

hydrolysed to indoxyl in the dyeing process. Oxidation, usually by exposure to air, turns the indoxyl to indigotin (or indigo blue), which is insoluble in water, ether and alcohol. Other dyes such as indirubin and kaempferol may also be present in these plants. Most industry analysts believe that there will always be a comparatively high demand for indigo dyes, and they are the most important dyes in terms of volume. At least 30 different means of synthesising indigo are currently known, with the most commonly used synthetic method yielding about 94%, compared to about 60% for *Indigofera*, the best natural source available (Clark *et al.*, 1993). The synthetic product is known as C.I. Vat Blue 1, C.I. Number 73000; the natural product as C.I. Natural Blue 1, C.I. Number 75780. The colour produced by the two products differs slightly because natural indigo also usually contains other dye chemicals (such as indirubin, indigo brown, indigo gluten and indigo yellow).

### 11.3.11 Chlorophyll pigments (green pigments)

Chlorophyll is the major pigment used by plants for capturing light energy. A chlorophyll molecule consists of a porphyrin head (four pyrrole rings containing nitrogen arranged in a ring around a magnesium ion) and a long hydrocarbon tail. The hydrocarbon tail is lipid-soluble. There are four types of chlorophyll: chlorophyll a, found in all higher plants, algae and cyanobacteria; chlorophyll b, found in higher plants and green algae; chlorophyll c, found in diatoms, dinoflagellates and brown algae; and chlorophyll d, found only in red algae. The dye is extracted from natural sources (usually stinging nettle, spinach, alfalfa or corn) and used extensively in colouring inks, resins, soaps and waxes, edible fats, cosmetics, liniments, lotions, perfume, mouthwashes and leather. The dyestuff is known as C.I. Natural Green 3, C.I. Number 75810. It is very difficult to prepare pure chlorophyll chemically and the commercial product contains a mixture of chlorophylls a and b (in the ratio of 3:1) and several carotenoids. The commercial process for extracting chlorophyll from plant material involves many steps using solvents such as petroleum ether and acetone.



### 11.3.12 Phycobilins

These are accessory pigments that red algae and cyanobacteria use to aid in the capture of light energy. Three of the four known phycobilins are involved in photosynthesis: phycoerythrin (phycoerythrobilin), phycocyanin (phycocyanobilin) and allophycocyanin (allophycocyanobilin). In structure they are similar to the chlorophylls but are linked to a protein. Phycobiliproteins appear as red or blue pigments and are being investigated as possible colourants for foods and cosmetics. The fourth phycobiliprotein is phytochrome, which also is very important in higher plants as a light receptor, especially in plant development.

### 11.3.13 Other dyes

Other dyes include diaroylmethane curcumin (from turmeric), pterocarpan (from sanderswood), the neoflavonoid berberine (from barberry and mahonia) and *Ocimum sanctum* (from Tulsi leaves) (Patel and Patel, 2006).

### 11.3.14 Lichens and fungi

Lichens are composite organisms of fungi and algae, and have long been used for dyeing textiles. The colours obtained from the dye-bearing lichens range from oranges, yellows and browns to reds, pinks and purples. They tend to grow slowly and only in unpolluted conditions, so their use on a large scale for colourants would not seem to be ecologically desirable or sustainable. However, their dyes are substantive, extremely fast to light, washing and salt water, and generally require a short, simple extraction process. Species of particular value include *Cladonia impexa* (containing usnic acid), *Evernia prunastri*, *Hypogymnia physodes*, *Lobaria pulmonaria*, *Ochrolechia parella*, *Ochrolechia tartarea*, *Paramelia omphalodes*, *Paramelia saxatilis*, *Rocella tinctoria* (used as a substitute for royal purple when the industry based on the shellfish species collapsed), *Umbilicaria pustulata* and *Xanthoria parietina*. Knowledge of the dyes present in or produced by lichens is currently relatively limited. The colour range suggests similarity to the anthocyanins and other flavonoids but their fastness indicates otherwise. Similarly, little is known about the colourants present in fungi but, in most cases, the colour is restricted to the epidermis. It seems likely that the colourants produced by lichens derive wholly or principally from the algal element of the organisms. Lichens may be difficult to work with but the qualities of the dyes that could be produced make them worthy of study, with the aim of developing suitable and economically viable uses and applications. *Monascus* fungi have long been used in parts of Asia to colour foods such as rice, wine and soybean

products (Jacobson and Wasileski, 1994). The pigments can be extracted and then modified to produce red pigments that can be used as food colourants. They can also be used directly by growing the mycelium on a food.

## 11.4 Chemistry and types of mordants

Natural dyes are either substantive, meaning that they do not require a mordant, or adjective, meaning that a mordant is required. Adjective dyes only dye materials which have been mordanted with a metallic salt or with the addition of a metallic salt to the dyebath itself. Examples of such dyes are logwood, madder, cochineal and fustic, among others (Gupta, 1990). In their pure state, adjective dyes are generally only slightly coloured and produce poor results when used alone.

Mordants (from Latin *mordere*, 'to bite', because the mordant eats away the surface of the fibre so that the dye can seep in) are chemicals in the form of metallic salts which are generally used to create an affinity between the fibre and the pigment. The main objective of the mordant when used with adjective dyes is to open up the pores so that the colourant can penetrate the fibres, thereby helping in the fixation of the dyestuffs on the substrate. However, mordants can also be used with dyes which may be applied directly. In this case their function is to form an insoluble compound with the dyestuff within the fibre itself, thereby improving the fastness properties of the dyed material.

Mordants can broadly be classified into three categories:

1. Metal salts or metallic mordants
2. Tannins and tannic acid
3. Oils or oil mordants.

Cotton can be treated with these mordants and can thus acquire an affinity for basic dyes. Tannic acid and oil mordants also act as primary mordants for metallic salts. For instance, cotton mordanted with tannic acid is able to absorb all types of metallic mordant and can be readily dyed with mordant dyes. In such cases, the metallic mordant forms complexes with the carboxylic groups of tannic acid (Nalankilli, 1997). In short, mordants can be considered as an integral part of the natural dyeing process.

### 11.4.1 Metallic mordants

Naturally occurring metal salts were once used as mordants in order to ensure reasonable fastness of colour to sunlight and washing. Today, metal salts of aluminium, chromium, iron, copper and tin are also used. Some of the important metallic mordants are alum, potassium dichromate, ferrous sulphate, copper sulphate, stannous chloride and stannic chloride.

Most natural dyes are able to form metal complexes (Bhattacharya and Shah, 2000) and thereby produce different shades (hues). Therefore virtually all types of metal salts can in fact be used for this purpose. However, some restrictions on the use of metal salts were drawn up in the EC Control of Substances Hazardous to Health Act, 1989. The maximum permissible amounts of different metals in the final product are as follows (Ansari and Thakur, 1999):

As (1 ppm), Cd (2 ppm), Co (4 ppm), Cr (2 ppm), Pb (1 ppm), Cu (50 ppm), Ni (4 ppm), Zn (20 ppm).

However, the upper limits set for the presence of metals vary between products and are invariably dependent upon the eco-standard chosen. Fortunately, there is no upper limit on aluminium, iron and tin, and the limit on copper is also fairly high. So, these salts can be safely used for complexing (Chavan and Chakraborty, 2001) and mordanting but their quantities should be optimised so as to minimise pollution.

#### 11.4.2 Tannins and tannic acid

Tannins are important in processes that use natural dyes producing yellow, brown, grey and black colours. They also improve the affinity of fibres to different dyes. Tannins are mainly used in the preservation of leather, glues, stains and mordants. Vegetable tannins are bitter and astringent substances that occur as excretions in the bark, leaves, fruits, galls, etc. of plants. These excretions may be used directly or in concentrated form (Raja and Thilagavathi, 2008). Tannins are naturally occurring phenolic compounds of high molecular weight (ranging from 500 to 3000). The phenolic hydroxyl group allows them to form effective cross-links between proteins and other macro-molecules. Tannins which contain o-dihydroxy (Catechol) group can form chelates, which give different colours with different metals.

Numerous tannin-containing substances are employed as mordants in the dyeing of textile fibres. Vegetable tannins are divided into two distinct classes – hydrolysable tannins and condensed tannins – according to the type of phenolic nuclei involved and the manner in which they are joined together.

##### *Hydrolysable tannins*

These tannins are distinguished by having a polyhydric alcohol, such as glucose, as the core. The hydroxyl groups of this alcohol are esterified either partially or wholly by gallic acid or its cogener. Such tannins are readily hydrolysed by acids, bases or enzymes, creating carbohydrates and a number of isolable crystalline phenolic acids: thus they are known as hydrolysable

tannins. The other acid isolated from these tannins is ellagic acid. Some of the important raw materials for these tannins are Myrabolan fruit (*Terminalia chebula*), oak bark and wood (*Quercus alba* and other species), Sumach leaves (*Rhus typhina*), gall nuts (*Quercus infectoria*) and pomegranate rind (*Punica granatum*). Myrabolan and sumach contain ellagitannic acid and gallotannic acid respectively, while gall nuts contain 60–77% tannic acid. When left to stand for a long period, the aqueous solution of tannic acid decomposes by fermentation, which can be inhibited by the addition of boric acid. The alkaline solution of tannic acid rapidly absorbs oxygen from the atmosphere, and then turns brown due to decomposition.

### *Condensed tannins*

Tannins of this class contain only phenolic nuclei. When treated with a hydrolytic reagent, particularly in an acid solution, they show a tendency to polymerise into insoluble, amorphous red coloured compounds known as phlobaphenes. These tannins are mostly formed by the condensation of two or more molecules of flavon-3-ols, specifically catechin. Catechin was first isolated from the tannins of *A. catechu* by Runge, 140 years ago (Patel, 2009). It produces copper red colours on cotton, wool and silk with superior washing and light fastness.

### 11.4.3 Oil mordants

Oil mordants are mainly used in dyeing processes using madder, producing Turkey red colour. The main object of the oil mordant is to form a complex with alum, which is used as the principal mordant. Alum is soluble in water and does not have affinity for cotton, so is easily washed out from the treated fabrics. The naturally occurring oils contain fatty acids such as palmitic, stearic, oleic and ricinoleic acid, and their glycerides. The  $-\text{COOH}$  group of fatty acids react with metal salts and are converted into  $-\text{COOM}$  (M denotes the metal; for example, in the case of alum salts, aluminium). It has also been found that when concentrated sulphonic acid is treated with oils, sulphonated oils are produced, which have better metal binding capacity than natural oils, due to the introduction of the sulphuric acid group  $-\text{SO}_3\text{H}$ . This can react with metal salts to produce  $-\text{SO}_3\text{M}$ . The bound metal can then form a complex with a mordant dye such as madder, producing a Turkey red colour with superior fastness and hue.

## 11.5 Application of mordants to textiles

Metallic mordants are soluble in water and are only loosely held by cotton fibres. These mordants must therefore be precipitated onto the fabric by

one of two methods: conversion of the mordants into insoluble form and treatment of the fibres with oil or tannic acid, followed by impregnation of the treated fabric with a mordant solution. In the latter method, the metallic mordants are fixed to the cotton by oil or tannic acid. Alum is a widely used mordant for cotton; the addition of an alkali to an alum solution produces aluminium sulphate, which is also used as a mordant, and is extensively used for dyeing of Turkey red colour on cotton. For the successful application of chrome mordant, it is essential that dichromate is reduced to chromic oxide before the mordanted material is dyed. When the goods are treated with dichromate after dyeing, the chromic acid produced acts as an oxidising agent, and the chromic oxide which is generated in this manner acts as the mordant. Iron salts are very widely applied as mordants in dyeing and printing, and are generally used with tannin-treated cotton fabrics. Copper salts are used in cotton dyeing as oxidising agents for the production of cutch browns and logwood blacks. Copper sulphate is frequently employed in the dyeing of black shades on cotton and for this purpose it is generally fixed with the help of tannic acid. Tin mordants produce exceptionally brilliant colours.

Stannous salts are very powerful reducing agents and are usually used in discharge printing. Due to their powerful reducing action, they cannot be used in conjunction with an oxidising mordant such as copper sulphate. Tin mordants should not be used with natural dyes that are susceptible to reduction, as they may become decolourised, and stannous salts are not frequently employed as mordants on cotton. Persian berries yield a good yellow to orange shade on materials previously mordanted with tannin and stannous chloride. Stannic salts are extensively used as mordants for cotton, with many natural dyes including logwood, fustic, quercitron and weld fixed on cotton with stannic oxide produced on mordanting.

Wool is more receptive to natural dyes and mordants than cotton. It can absorb both acids and bases effectively due to its amphoteric nature. When treated with a metallic salt, wool hydrolyses the salt into an acidic and a basic component. The basic component is absorbed at the  $-\text{COOH}$  groups while the acidic component is removed in the course of washing. Aluminium sulphate is quite effective as a mordant for wool and is sometimes used without the addition of other substances. However, when used along with tartar (tartaric acid), full depth of shade and brilliant colours are obtained, which also have good rubbing fastness. For full depth of shade, about 6–8% aluminium sulphate and 5–7% tartar are necessary. On the other hand, alum is less effective as a mordant for wool than aluminium sulphate. Due to low cost and ease of application, the mordanting of wool with sodium or potassium dichromate is widely adopted as a technique. This provides full bright shades with fairly good fastness properties. The brightness of the shade can be further improved by addition of an organic acid such as formic, oxalic or

tartaric acid. Ferrous sulphate is not very frequently used as a mordant for wool. Copper sulphate is used in conjunction with aluminium sulphate and ferrous sulphate in the dyeing of logwood blue and logwood black. Among the tin salts, stannous chloride is used as a mordant for wool.

Silk possesses similar amphoteric properties to wool and can absorb both acids and bases. However, wool contains a thiol (SH) group (present in the cystine amino acid), while silk does not. This means that potassium dichromate can be used with wool, but not with silk: in wool, the thiol group helps to reduce the hexavalent chromium in potassium dichromate to a trivalent form which can then form a complex with the fibre and the dye, while no such process can occur with silk due to the absence of the thiol group. Alum is not a preferred mordant for silk since it diminishes its lustre and pliability. Iron salts are also used both for mordanting and weighing of silk, with excellent black colours produced on iron mordanted silk. Finally, stannous chloride is regarded as one of the most important mordants for silk and can also be used as a weighing agent.

## 11.6 Application of natural dyes to textiles

In the textile industry, modern dyeing processes and machinery are designed for use with synthetic dyes. Natural dyes, used in traditional ways, generally offer less consistent performance, and several require the use of additional chemicals that are potentially hazardous to the environment and require control procedures. Table 11.1 presents some important applications of natural dyes to natural as well as synthetic fibres. Synthetic dyes have been designed to give good results on both artificial and natural fibres. Many natural dyes, on the other hand, do not perform well with artificial fibres. However, some studies are available (Gupta *et al.*, 2004; Lokhande and Dorugade, 1999) that report the successful application of natural dyes onto natural and synthetic textiles using modern dyeing techniques such as open bath, high temperature high pressure (HTHP) and padding techniques (Patel *et al.*, 2002; Patel *et al.*, 2003). In these methods the amount of dye used to produce a desired shade is less than in conventional methods for natural dyes. Other studies have shown that reuse of the dyebath during dyeing with natural dyes not only substantially decreases the amount of dyeing effluent but also offers savings in terms of dye cost and energy. The reused dyebaths show consistency in shades, indicating that it may be possible to achieve effluent-free dyeing with natural dyes. Another method to improve colour depth is the multidip method: this results in much deeper shades that could not be achieved through any of the single dip (exhaust) methods. The use of various unconventional techniques such as microwave, sonicator (Vankar *et al.*, 2008), ultrasound and supercritical carbon dioxide are reported to make natural dyeing more eco-friendly.

Recently, eco-friendliness has become an important consideration worldwide. The major obstacle to environmentally friendly dyeing is the use of coal tar products in various operations of textile wet processing, some of which have come under criticism for causing environmental pollution and health hazards. It is thus important to replace those dyes and chemicals that contain coal tar with more environmentally friendly products obtained from natural resources. At present articles finished with natural antimicrobial agents (Patel and Tandel, 2005), such as fishing nets, fall into a small niche market fed by craft workers and small commercial firms; however, what is a small niche market today could become a larger market in the future, as has occurred with herbal teas and natural cosmetics. There has been little effort to define and predict the market for natural products that possess colouristic as well as antimicrobial properties (Singh *et al.*, 2005).

### 11.6.1 Processes and machinery

In craft dyeing the dyes are extracted from the plants by soaking in water, alkali, alcohol or another organic solvent. Heat may also be required. For some dyes a multistage process may be needed, with the dye product(s) not required extracted by using sequences of different solvents as a first step. Alternatively, the fibre may be dyed with the whole plant extract and then treated with a mordant to change the colour of one of the dyes. Craft dyeing nearly always uses the vat process, which is the traditional way in which natural plant dyes have been used. Other techniques are also used by industrial dyers. The production of textiles requires the use of large volumes of water but it has been estimated that the dyeing process alone can use as much as 70% of the total water consumption involved (Watson, 1991). About 20 000 L of water can be needed to process 1 tonne of wool from the raw material to the finished textile. Most natural dyes need to be extracted into water, and usually with heat. It is not clear how the current commercial machinery and dyeing processes would need to be adapted to use natural dyes.

Three different methods are used for dyeing textiles on a commercial scale:

1. The dye liquor is moved and the material remains stationary, as in raw stock or package-machine dyeing.
2. The textile material is moved through the dye liquor, as in chain warp dyeing, jig dyeing, beck dyeing and continuous dyeing, which is used for most woven materials except for stretch fabrics.
3. The textile material and the dye liquor both move, as in the Klander-Weldon skin dye machine, and jet dyeing. Chain warp dyeing is widely used in the dyeing of indigo on warp yarns in the form of ropes or chains. Several chains are pulled through the bath at a time. The technique is

useful for dyeing small or test batches, and used widely for material that is easily stretched. Jet dyeing has the advantage of using smaller volumes of dye liquor than several of the other processes.

The major dyeing techniques used are exhaust dyeing (using 1 or 2 above), continuous dyeing (used for most vat dyes), pigment dyeing (using finely dispersed pigments) and solvent dyeing (using non-aqueous media and more efficient than aqueous dyeing although with potentially greater operator and environmental hazards). Some dyeing methods are more suitable for fabrics, while others are better suited to stock yarn.

## 11.7 Fastness properties of natural dyes

Generally, materials dyed with natural dyes do not possess the same excellent fastness properties exhibited by synthetic dyes. Although mordanting and after-treatments help to improve fastness, the intrinsic susceptibility of the chromophore of natural colourants to photochemical degradation results in low fastness to washing and light. From the historical sources available, it is clear that there was an early awareness of the fleeting nature of natural dyes and significant attempts were made to improve or restore their fastness properties (Taylor, 1986). Early attempts were made to correlate the chemical constitution of dyes with their light fastness and it was claimed that the fastness to light depended on the number, nature and position of the substituent groups on the dye chromophore. However, it was later discovered that light fastness is a complicated phenomenon and cannot be related to the invariable effect of substituent groups in a dye molecule. Several other factors which affect the light fastness of natural dyed materials are (Sekar, 1999) as follows:

- Chemical structure of the colourant
- Concentration of the dyestuff
- Nature of fibre
- Nature of incident light
- Composition of surrounding atmosphere
- Effect of mordants
- Presence of foreign materials.

Poor washing fastness of many natural dyes is mainly due to the following factors:

- Weak bond between natural dye and fibre
- Change in hue due to the breaking of the dye–metal complex during washing
- Ionisation of natural dyes during alkaline washing.



The washing fastness of some natural dyes can be improved by a post-treatment with alum or a dye-fixing agent resulting in the formation of a dye-fibre complex or a cross-link between the dye and fibre, respectively (Gupta, 1999). The fastness properties of a few natural dyes are discussed below.

### 11.7.1 Natural yellow dyes

Vegetables yellow dyes generally have low tinctorial value and the shades are pale. They consequently fade more quickly, depending on the mordant used during their application. Aluminium and tin mordants cause more light fading than chrome, iron or copper mordants, as in the case of onion, tesu, etc.

Flavonoids constitute a major class of natural yellow dyes. The basic flavonoid chromophore is susceptible to photochemical attack and probably leads to the formation of quinones. Consequently, the yellow colour turns to a dull brown as commonly seen in old textiles in museums (Crews, 1982).

The nature and position of the substituent group on the chromophore as well as their number also affect intensity and light fastness. For example, flavonic pigments present in weld, sandalwood and plumes exhibit a light fastness rating which is much higher than that of flavonol pigments, such as those present in quercitron, Persian berries and onion skin. This is due to the presence of a highly photosensitive hydroxyl group in position 3 in flavonic pigments. Turmeric is the most brilliant natural yellow dye available to date. Despite being subject to light-induced fading, it continues to be used for its brilliance. Berberis is a basic dye and, as it fades quickly when exposed to light, has a light fastness grade of 1 (Duff *et al.*, 1985). In this case, the ammonium group, which imparts the basic dyeing property, is probably responsible for its photosensitivity, which is further increased by fluorescence.

Anthraquinonoid-based yellow and orange mordant dyes, such as rhubarb, manjith, morinda, madder, chayroot, and so on exhibit very good fastness to light. These colours are quite resistant to photofading due to the presence of an anthraquinone chromophore which is intrinsically resistant to light fading. The wash fastness properties of yellow dyes range from fair to excellent.

### 11.7.2 Natural red dyes

Natural red dyes are mostly resistant to light and washing, but sometimes the choice of mordant may affect the washing fastness. For instance, the washing fastness of cochineal dyed wool is much higher when chromium acetate mordant is used than when alum mordant is used. Hydroxyanthraquinone

pigments, the most important sources of red dyes (both plant- as well as animal-based), possess good fastness to light. These compounds form stable metal complexes with several mordants, yielding a wide range of deep and fast shades. Mordants usually affect the fastness of anthraquinone-based dyes such as cochineal and kermes: when used with alum these have a light fastness grade equal to 3, whereas with tin mordant, the light fastness is improved to 5–7. The nature of the substrate also affects the light fastness of these dyes (Venkatraman, 1952). Red dyes based on pigments other than anthraquinones, such as sappanwood safflower, sandalwood and canwood, have poor light fastness.

### 11.7.3 Natural blue dyes

Indigo produces the most brilliant and fastest blue shades on all fibres. The washing fastness of indigo is excellent since it is applied in soluble leuco form which oxidises to insoluble form inside the fibre which then holds it firmly. An unusual feature of the photochemical behaviour of indigo is that its light fastness on wool is slightly higher than that on silk and much higher than that on cotton.

### 11.7.4 Natural brown dyes

Browns are generally obtained from quinone-based dyes. Naphthoquinones have only moderate fastness, while anthraquinone-based browns have excellent fastness due to the stability of the dye chromophore. Copper and iron salts are sometimes referred to as ‘saddening’ agents since they tend to turn the colours to dull and deep shades, particularly browns. Both these mordants enhance the light fastness of dyes. Some yellow dyes such as *dolu* give deep rich browns when mordanted with copper salts. Tannins combine with ferrous salts to form complexes which give a range of grey-brown shades.

### 11.7.5 Natural black dyes

Anthraquinone-based cochineal dye produces a black shade on protein fibres with moderate light fastness, but this dye is no longer used. Silk can be dyed deep black through the use of logwood dye on an iron tannate mordant. This method is popular even today, with logwood considered excellent for providing depth and fastness on most natural and synthetic fibres (Schweppe, 1992).

Tannins are an important source of black dyes. Pomegranate rind contains the hydrolysable tannin flavogallol, which combines with iron salt to produce deep black shades with excellent light fastness.

## 11.8 Future trends

In this new millennium, the maintenance of a safe environmental balance will increasingly be necessary. Natural dyes had been neglected for about 150 years, but have recently come back into the limelight. Thus, the natural dyeing of different textiles has been practised mainly in minor sectors for speciality products, with synthetic dyes used in larger sectors for general textiles/apparels owing to the specific advantages and limitations of both natural dyes and synthetic dyes. Moreover, commercialisation of the cultivation of the plants from which most natural dyes are generated will certainly assist in preserving the ecological balance. These vegetable resources are not only sustainable but also biodegradable, while the petrochemical sources of synthetic dyes are both limited and irreplaceable. There has also been a great deal of recent interest in the pharmacological effects and possible health benefits of the use of natural dyes. However, the main requirement for their revival on a commercial scale is the development of new techniques which are effective enough to allow the natural dyes that are available to be used to maximum effect. Future studies should focus more on improving the fastness properties and widening the range of shades available from natural dyes, with more research certainly required if the market is to be developed to its full potential.

## 11.9 Sources of further information and advice

Extensive research is currently being carried out worldwide on the extraction of natural dyes and their application to textiles using modern scientific techniques. Textile scientists must also search new sources and standardise the application methods of natural dyes to textile substrates in order to improve their effectiveness and market potential. There is currently a need to study the effect of various metallic mordants and of different mordanting techniques on the strength and hue of the colour obtained in both natural and synthetic fibres when these are dyed using natural colourants, applied with scientific techniques and machinery.

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**Abstract:** Structural characteristics and classification of direct dyes are discussed. The chemistry of direct dyes belonging to azo, azine, copperphthalocyanine and other classes are discussed. Chemistry of benzidine-free direct dyes and after-treatment dyes is also discussed.

**Key words:** azo dyes, phthalocyanines, triphenodioxazines, substantivity, cellulosic substrates

## 12.1 Introduction

Direct dyes are inherently substantive to cotton and other cellulosic substrates. Their aqueous solutions dye cotton generally in the presence of an electrolyte such as sodium chloride or sodium sulphate. Historically they replaced naturally occurring mordant dyes. Direct dyes are the most important single class for cotton in the sense that they are simple to use. Optimum conditions vary, but dyeing is usually carried out at or near boiling point in the presence of an electrolyte such as sodium chloride or sodium sulphate.

Direct dyes are relatively inexpensive. They are available in a full range of hues but are not of high colour brilliance. They show poor to moderate fastness to washing. They are therefore used on materials where good fastness is not of prime importance. The light fastness of dyeing with direct dyes on cellulosic fibres varies from poor to fairly good, although some copper complex direct dyes have very good light fastness. The light fastness of metallisable dyes can be increased by post-treatment with copper salts, and wash fastness can often be improved by resin treatment. Shades are generally affected by metal salts but less so by resins imparting crease resistance. As usual the deeper the dyeing colour, the lower the fastness is to wet treatments, and the higher the fastness to light.

Substantivity of direct dyes was initially attributed to secondary valence bonding between the dye and the fibre. The observation that coplanar molecules are always more substantive than nonplanar ones led to the coplanarity theory with the assumption that the coplanar dyes are in contact with the cellulose molecules along their entire length. The affinity was then explained as an outcome of the presence of hydrogen bonds (Boulton, 1951); however, such bonds are probably prevented by a water layer between fibre and dye (Rattee and Breuer, 1974). A very convincing explanation is as follows (Bach *et al.*, 1963). Single dye molecules are absorbed by the intermicellary

cavities of the cellulosic fibres and they form aggregates in these cavities. Because direct dyes become aggregated in aqueous solutions at normal temperatures, substantivity is initiated only at higher temperatures since the diffusion is possible only at higher temperatures. Direct dyes are therefore characterised by their tendency to aggregate and therefore they need to be coplanar.

The affinity or substantivity of direct dyes for cellulose fibres depend on the type of chromophore and can also be influenced by the choice of dyeing conditions. They invariably contain solubilising sulphonic acid groups that are ionised in aqueous solution. The dye molecule exists in the dyebath as the anion, and thus an electrolyte must be added to the dyebath because cellulose fibres have a negative charge on the surface in water. The cations of the electrolyte neutralise the negative charge and help the aggregation of dye anions on the fibre which is called salting out effect. With the help of Freundlich or Langmuir adsorption isotherms exothermic adsorption can be described (Porter, 1993). After adsorption, dye molecules diffuse from the surface into the amorphous areas of the cellulose fibre. Again, the rate of dyeing can be controlled by the dyeing parameter. The diffusion process is in general understood in terms of Fick's law (Brady, 1992). The dye–fibre interaction can be described by hydrogen bonds or van der Waals forces (Lewis, 1998). The strength of these bonds is low, so that the dyes can be washed out of the fibre again. At dyeing equilibrium, the rate of absorption is equal to the rate of desorption. In addition treatment improves the longevity of the dye on the fibre.

Direct dyes usually cannot meet today's more stringent wet fastness requirements for apparel and linens. Recently their share in the market has gradually declined in favour of the reactive dyes, which have often very good washing fastness and have bright hues. Only in individual cases do direct dyes achieve the brilliance of reactive dyes. The light fastness of direct dyes covers the entire scale from one to eight, meeting even the highest requirements. With increasing depth of shade the wet fastness decreases to such an extent that dyeing must generally be after-treated. The majority of direct dyes are characterised by excellent affinity to the fibre.

## **12.2 Classification of direct dyes according to dyeing characteristics**

Direct dyes with similar chemical constitutions can have quite different application and fastness properties (SDC, 1982). They also vary widely in their dyeing behaviour creating problems of compatibility. Grouping of direct dyes according to their dyeing properties is therefore more practical. The classification by the Society of Dyers and Colourists (SDC) is based on their levelling ability and their response to increase the dyeing temperature and to added salt during exhaust dyeing.



### 12.2.1 Society of Dyers and Colourists (SDC) class A direct dyes

These are self-levelling dyes with good migration even in the presence of salt. Their substantivity is lower and hence usually requires considerable amounts of electrolytes for good exhaustion. These dyes are relatively of low molecular weight mono- and bisazo dyes with several anionic sulphonate groups per molecule. Thus they have good solubility in water and do not aggregate to a significant degree in solution. Dyeing in the presence of added salt is started usually at 50°C, the bath heated to the boil over 30–40 min, and dyeing continued at the boil for up to 1 h. In order to promote exhaustion several further additions of salt are necessary depending upon the depth of shade and the liquor ratio. Although these dyes would give greater exhaustion at lower temperatures of dyeing, dyeing at the boil allows good levelling and adequate penetration of the dye into the cellulosic substrate.

### 12.2.2 SDC class B direct dyes

These dyes are shock-sensitive dyes and hence salt-controllable with poor levelling characteristics. Compared to class A dyes they are of high molecular weight. Most of them are bis- and trisazo dyes with fewer number of sulphonate groups per molecule. They have low to moderate substantivity in the absence of salt but exhaust well on the addition of small amounts of salt to the dyebath. The dyeing method is similar to that of class A dyes but initial addition of salt is not necessary. The exhaustion is controllable by the addition of dissolved salt at boil.

### 12.2.3 SDC class C direct dyes

These dyes exhibit poor migration and are very salt-sensitive dyes. Levelling is controlled by the gradual increase of the dyeing temperature, subsequent additions of limited amount of salt and levelling agents if required. They are also temperature-controllable. Dyeing is started in the absence of salt at low temperature, and the dyebath is slowly heated, with particular care in the temperature region where exhaustion is more rapid. Some salt may be added during further dyeing at the boil. Majority of these dyes are often polyazo dyes with few sulphonate groups and of high substantivity to cellulose. They are very prone to aggregation in solution and sensitive to salt addition particularly at lower temperatures of dyeing. At low temperatures presence of salt in the dyebath impedes exhaustion because it promotes more aggregation of the dye; the lower the concentration of the dye molecules in the solution that can diffuse in to the substrate, the lower the rate of dyeing. Dye aggregates are too large to penetrate into the pores of cellulose fibres.

A careful examination of the structural features of direct dyes from the three groups reveals that in passing from group A to group C, the dye substantivity generally increases because of increased molecular weight and a lower number of sulphonate groups per dye molecule. Class C dyes are therefore of better washing fastness than class B dyes. Class A dyes have even lower fastness.

## 12.3 Classification based on chemical structure

### 12.3.1 Azo dyes

Anionic azo dyes constitute the major proportion of the direct dyes. The following structural features are necessary for higher substantivity.

In the planar and conjugated double-bond system coplanarity and conjugation are increased simply by the introduction of more azo groups. The importance of coplanarity is shown by the example of 4,4'-diaminodiphenyl derivatives. Whereas 3,3'-disubstituted diaminodiphenyl derivatives (e.g. *o*-tolidine or *o*-dianisidine) as diazo components produce highly substantive dyes, the substantivity is not found in 2,2'-disubstituted derivatives. In the latter case the coplanarity is no longer possible.

In addition to the aromatic ring bridges such as  $-\text{CH}=\text{CH}-$  are found in dye molecules ensuring long chains of conjugated double bonds (Schirm, 1935). Exceptions to this rule are the bridges  $-\text{NHCONH}-$ ,  $-\text{CONH}-$ , and  $-\text{NH}-$  which increase substantivity in spite of the interruption in the conjugated system. In these structures the substantivity originates from the ability to form hydrogen bonds. Other groups creating an interruption in the conjugated biphenyl systems like  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CO}-$ ,  $-\text{SO}_2-$ ,  $-\text{S}-$  and cyclohexylene lower the substantivity of the linked segment alone remains associated with the dye.

#### *Monoazo direct dyes*

With the exception of sulphonic acid derivatives of 2-(4'-aminophenyl)-6-methyl benzothiazole as diazo component, the so-called dehydrothio-*p*-toluidine (1), substantive monoazo dyes are of no practical importance as direct dyes.

Compound 1 is obtained by melting *p*-toluidine with sulphur at 130–230°C. The derivatives 2–5 are used to produce monoazo direct dyes. Dehydrothio-*p*-toluidine monosulphonic acid (2) and dehydrothio-*p*-toluidine disulphonic acid (3) are obtained by the sulphonation of 1 with oleum. Primuline base (4) and the higher homologue (5) are found in a mixture with (1) during the sulphur melting process and are separated by vacuum distillation.

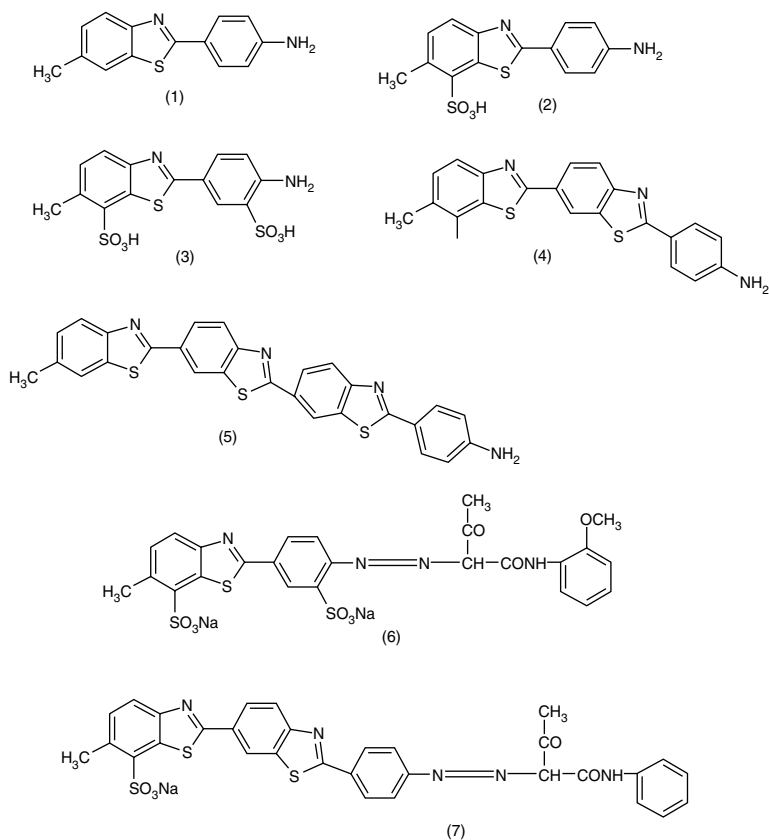
Diazotisation of (3) and coupling to acetoacetic acid *o*-anisidide results in the lightfast yellow (6), C.I. Direct Yellow 27, C.I. 13950 [10190-68-8]. Coupling of the diazotised monosulphonic acid of the primuline to

acetoacetic acid anilide gives the clear, greenish yellow (7), C.I. Direct Yellow 22, C.I. 13925.

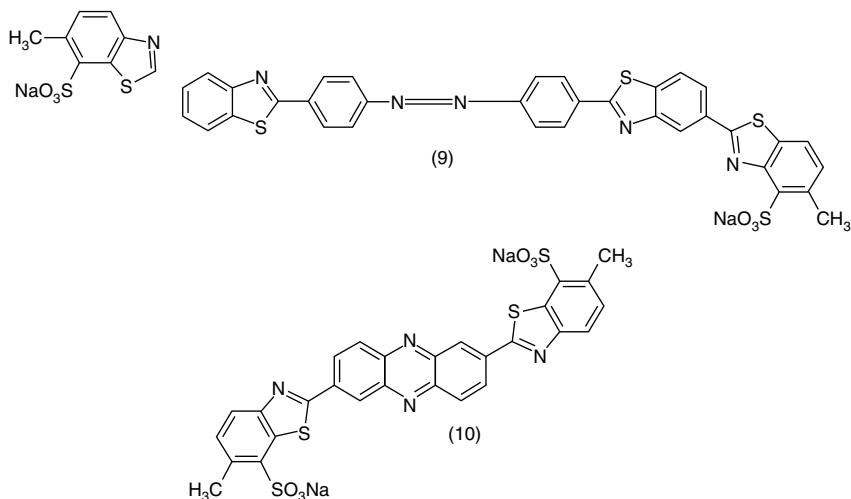
Substantive monoazo dyes with very good light fastness are obtained by oxidation of (1) and its derivatives. The dye (8), C.I. Direct Yellow 28, C.I. 19555 [8005-72-9], discovered by H Pfitzinger is obtained by the oxidation of (1) with sodium hypochlorite. In the preparation of C.I. Direct Red 28, in addition to the azo dye diphenazines (10) are obtained as by-products, which in some cases have to be separated when they impair the shade and fastness properties of the dyes.

Oxidation of the sodium salt of the monosulphonic acid of the primuline base in the alkaline pH range with sodium hypochlorite gives the dye (9), C.I. Direct Yellow 29, C.I. 19556 [6537-66-2].

Other than the acetoacetic acid arylides, pyrazolone derivatives are also used as coupling components. Naphthol sulphonic acids are of only minor importance. Compound 2 and the sulphonated primuline base are also used as diazo components for certain orange disazo direct dyes (Figs. 12.1 and 12.2).



### 12.1 Monoazo direct dyes and their intermediates.



### 12.2 Intermediates for monoazo direct dyes.

#### *Disazo direct dyes*

In the case of disazo dyes it is necessary to distinguish between primary and secondary types. Primary disazo dyes are produced by bisdiazotisation of bifunctional disazo component D and coupling to two equivalents of coupling components C<sub>1</sub> and C<sub>2</sub>, or by reacting two equivalents of a diazo component with one bifunctional coupling partner; they are schematically represented respectively as C<sub>1</sub> ← D → C<sub>2</sub> and D<sub>1</sub> → Z ← D<sub>2</sub>. Depending on whether C<sub>1</sub> and C<sub>2</sub> or D<sub>1</sub> and D<sub>2</sub> are the same or different, symmetrical or unsymmetrical dyes are obtained.

The secondary disazo dyes are obtained from an azo dye carrying an amino group which can be diazotised. Thus, for the manufacture of secondary disazo dyes, diazotised amine D is coupled to an amine M with free *para* position, which in turn is diazotised and coupled to a coupling component. They are represented by D → M ← C.

#### *Primary disazo dyes of the type C<sub>1</sub> ← D → C<sub>2</sub>*

Primary symmetrical disazo dyes with benzidine as bis diazo component were long considered to be the prototype of direct dyes. In fact the commercial production of direct dyes for cotton started with the discovery of Congo Red, C.I. Direct Red 28, C.I. 22120 (11) [573-58-0] by Paul Boettiger in 1884. Subsequently 3,3'-disubstituted-4,4'-diaminodiphenyl derivatives with the structure 12 were considered to be the best bridging intermediates for symmetrical as well as unsymmetrical disazo direct dyes. Because of the carcinogenic properties of unsubstituted benzidine in humans (Barsotti and Vigliani, 1952; Case, 1954; IARC, 1975; Scott, 1952) and animal carcinogenicity of

substituted benzidines almost all major manufacturers worldwide stopped production of dyes based on these intermediates.

The other diamines developed as substitutes for the carcinogenic benzidine are represented by the structure (13). These diamines are also used in trisazo dyes.

Chrysophenine (14), C.I. Direct Yellow 12, C.I. 24895 [2870-32-8] is an example of direct dye using the diamine 13D. It is a very highly tinctorially strong reddish yellow with very good levelling properties. It is excellently suited for the dyeing of fabric blends like cotton-polyamide. It is obtained by coupling bisdiazotised 13D with two equivalents of phenol and subsequent ethylation.

The diamine 13E is used in the manufacture of C.I. Direct Red 75, C.I. 25380 (15) [2829-43-8]. Similar direct dyes with diphenyl urea group can be obtained from amino azo dyes by subsequent treatment with phosgene.

### *Substitutes for the carcinogenic diamines*

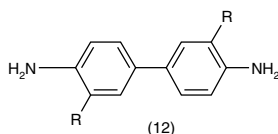
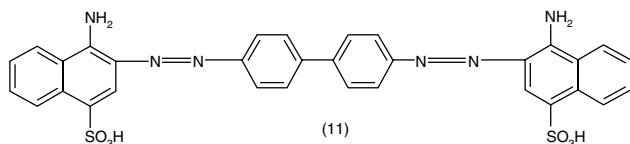
Recent research on direct dyes concentrated on the replacement of possibly carcinogenic benzidine (Shore, 1991). Although much of the human exposure to benzidines which led to bladder cancer was the result of handling the intermediate itself during the course of tetrazotisation, an appreciable level of exposure to these intermediates resulted from the use of crude dyestuffs which contained a free benzidine as an unreacted starting material. Furthermore, it is now well established that the ability of azo dyes to undergo reductive cleavage of the azo linkage could lead to an indirect route of exposure to an established carcinogen. Such a characteristic metabolism of azo dyes has been characterised using gut microflora (Chung, 1983; Hartmann *et al.*, 1978; Manchon and Lowery, 1965), liver enzymes (Idaka *et al.*, 1978), certain bacteria (Idaka *et al.*, 1978) and tissues containing the enzyme azo reductase (Juchau *et al.*, 1968). Further work in this area has been lucidly presented and through investigation it has been shown that 5,5'-diamino-2,2'-bipyridine is a possible replacement for benzidine (Calogero *et al.*, 1987). Considering the fact that cyclic aromatic five- or six-membered imides like phthalimide, benzimidazolone, quinoxalinedione and phthalazinedione possess the ability to form stable dimers by intermolecular hydrogen bonds several diamines containing cyclic amide groups have been evaluated as intermediates for synthesis of benzidine-free direct dyes (Szadowski and Niewiadomski, 1993, 1999). 3-[(4-Aminophenyl)-7-amino] quinoline has been evaluated as a substitute for benzidine (Krishnan *et al.*, 1986). The diamines 13B, 13C and 13B have been used to prepare disazo direct dyes in order to study the relationship between the structure and other properties (Chao and Chang, 1995). It has been shown that 13B gives dyes with superior properties (Chao and Chang, 1995). In order to ensure sufficient dye affinity to cellulosic fibres sulphonated benzanilide have been evaluated

as substitutes for benzidine (Czajkowski, 1991). The diamine 13C has been used to obtain mainly black direct dyes (Zhang *et al.*, 1999). The diamines 4,4'-diaminodiphenylsulphide (Chao and Pan, 1996) and 2,8-diamino-5,10-dihydro-10-hydroxy-5-methylphosphazine-10-oxide (Bello *et al.*, 2000) have been employed as diamines for obtaining green and black direct dyes.

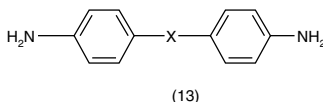
The benzidine congeners such as 3,3'-dimethylbenzidine, 3,3'-dichloro benzidine and 3,3'-dimethoxybenzidine are also carcinogens. With a view to reduce the mutagenicity of the benzidine congeners by introducing bulky substituents 2,2'-dimethyl-5,5'-dipropoxy benzidine has been synthesised and shown to be non-mutagenic (Bae and Freeman, 2001; Hinks *et al.*, 2000). A series of dyes has also been prepared using this diamine (Bae and Freeman, 2001; Hinks *et al.*, 2000) (Fig. 12.3).

*Primary disazo dyes of the type  $D_1 \rightarrow Z \leftarrow D_2$*

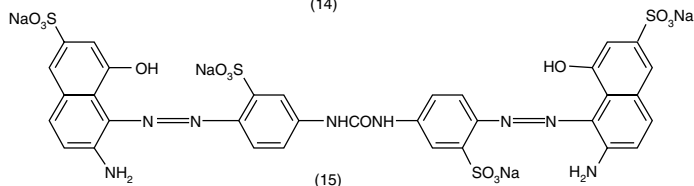
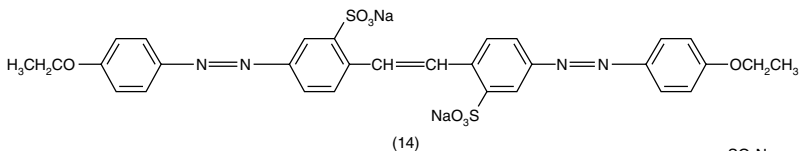
The most important coupling components for these dyes are Scarlet acid (16) and RW acid (17), resorcinol and m-phenylene diamine. The compound 16 is produced by treatment of J-acid with phosgene.



R = H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl  
 12A: R = H  
 12B: R = CH<sub>3</sub>  
 12C: R = OCH<sub>3</sub>  
 12D: R = Cl



13A: X = NH  
 13B: X = CONH  
 13C: X = SO<sub>2</sub>NH  
 13D: X = CH=CH  
 13E: X = NHCONH



**12.3 Bisazo direct dyes based on diamines.**

Examples are C.I. Direct Orange 26, C.I. 29150 (18) [3626-36-6], C.I. Direct Red 250, C.I. 29198 (19) and C.I. Direct Red 23, C.I. 29160 (20) [3441-14-3].

C.I. Direct Red 23 is obtained by simultaneous coupling of one equivalent each of diazotised aniline and 4-amino acetanilide with scarlet acid (J-acid urea). Although this dye possesses average fastness properties, it has special importance and because of its good levelling properties it is used for dyeing union fabrics, polyamide and chrome leather.

Coupling diazotised dehydrothio-p-toluidine sulphonic acid to resorcinol and subsequent coupling of diazotised aniline to the monoazo dye gives C.I. Direct Orange 18, C.I. 20215 (21). It is an important substantive dye. Primary disazo dyes of this type have attracted the interest of researchers in the context of development of benzidine-free direct dyes wherein a bifunctional coupler is prepared by the condensation of two moles of J-acid with one mole dichloride of the dicarboxylic acids like iso- and terephthalic acids (Wojciechowski and Gumulak, 2003; Wojciechowski *et al.*, 2003). Bifunctional couplers containing urea residues have again been subject of investigation, especially J-acid urea (Szadowski and Niewiadomski, 1999). Direct dyes containing two urea groups have also been made (Wojciechowski and Szadowski, 1999). Efforts in the synthesis of innovative bifunctional couplers continue (Hanna *et al.*, 2007).

#### *Secondary disazo dyes of the type $D \rightarrow M \rightarrow C$*

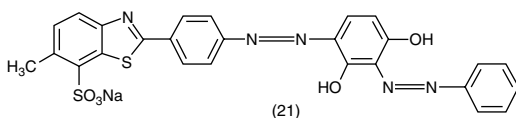
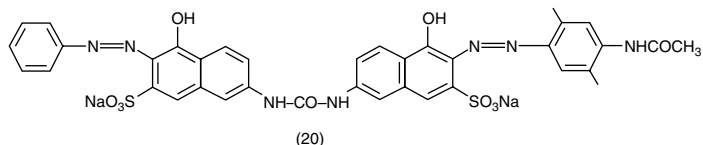
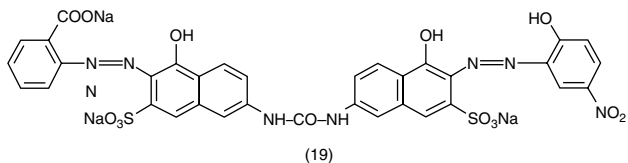
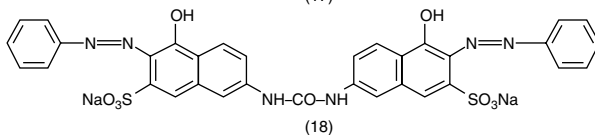
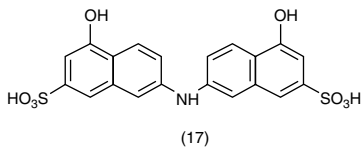
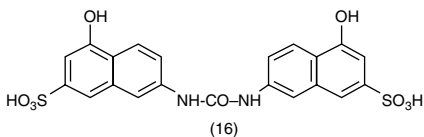
Dyes of this type mostly have a linear structure and often contain groups that enhance substantivity such as J-acid, J-acid derivatives, especially with acylated amino groups, urea bridges, or benzoylamino groups. The shade range obtainable in this group extends from orange through red, violet and blue to black (Figs 12.4, 12.5).

C.I. Direct Red 81, C.I. 28160 (22) [2610-11-9] is an important red dye belonging to this class. It is obtained from 4-aminoazobenzene-4'-sulphonic acid and benzoyl-J-acid.

C.I. Direct Black 51, C.I. 27720 (23) [3442-21-5] is obtained by coupling a mixture of diazotised 3- and 5-aminosalicylic acid to 1-naphthylamine and subsequent diazotisation followed by alkaline coupling to gamma acid.

#### *Trisazo direct dyes*

Blue, green and black grade dyes come from this class. 4, 4'-diaminobenzanilide (DABA) or 4, 4'-diaminodiphenylamine-2-sulphonic acid (DADPS) is used in place of benzidine. The structure is represented by the formula  $C \leftarrow D \rightarrow Z \leftarrow A$ . C.I. Direct Black 166, C.I. 30026 (24) and C.I. Direct Black 150, C.I. 32010 (25) are important examples in this class.



#### 12.4 Disazo direct dyes based on bifunctional couplers.

Trisazo dyes of the type  $A \rightarrow M_1 \rightarrow M_2 \rightarrow C$  are also very important. This group contains a number of dyes with good to very good fastness properties.

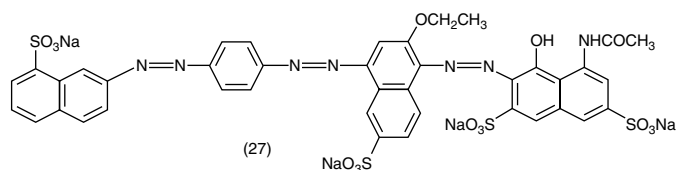
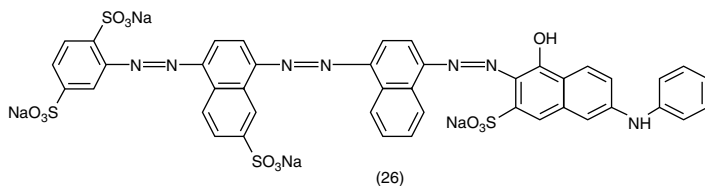
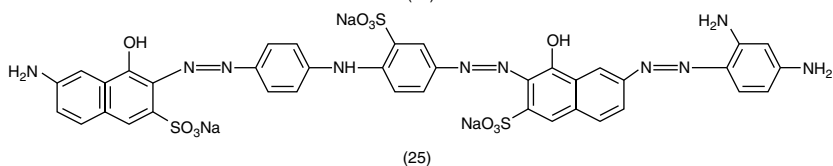
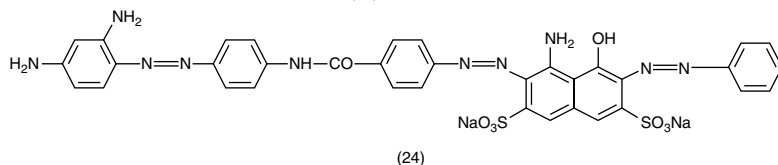
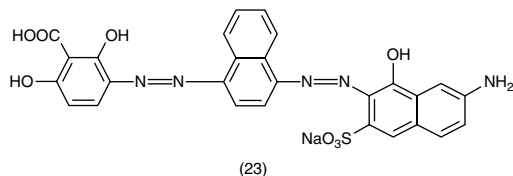
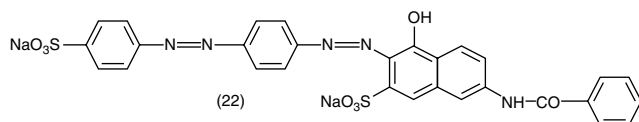
Aniline sulphonic acids are mainly used as the starting component A; cleve acids and 1-naphthylamine are used as middle components  $M_1$  and  $M_2$ . The final component C is from J-acid, N-aryl derivatives of J-acid, H-acid, gamma acid and their derivatives.

This group contains mainly black and green dyes. C.I. Direct Blue 78, C.I. 34200 (26) [2503-73-3] is an important example in this class. Another example is C.I. Direct green 33, C.I. 34270 (27).

#### *Tetrakisazo direct dyes*

These dyes are obtained by a further extension to the principles of trisazo dyes. They are mainly black dyes and only a few types are of industrial



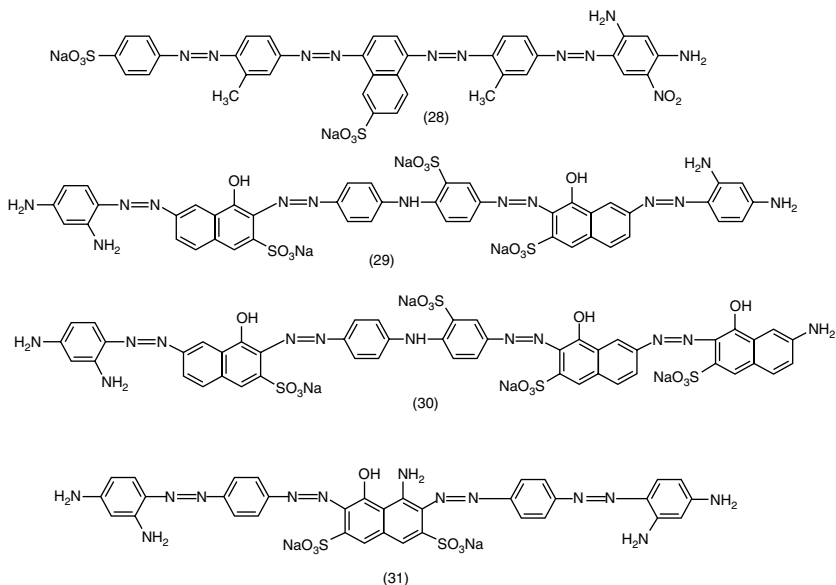


### 12.5 Bisazo and trisazo direct dyes.

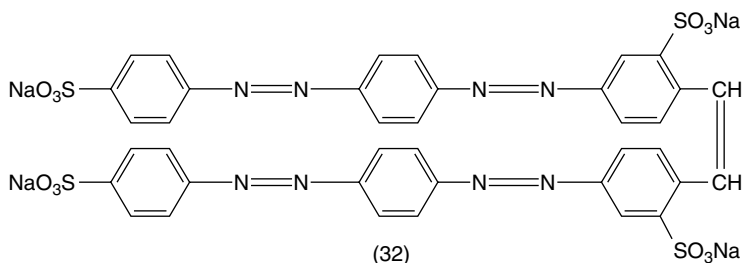
importance. Important types are  $A \rightarrow M_1 \rightarrow M_2 \rightarrow M_3 \rightarrow C$  and  $C \leftarrow Z \leftarrow D \rightarrow M \rightarrow C$ . An example of the first type is a brown direct dye C.I. 35850 [8002-98-0] (28). The second type of dyes are exemplified by C.I. Direct Black 22, C.I. 35435 (29) [6473-13-8]; C.I. Direct Black 151, C.I. 35436 (30) and C.I. Direct Black 19, C.I. 35255 (31) [6428-31-5]. Several polyazo dyes are listed in Colour Index (SDC, 1982) (Figs. 12.6 and 12.7).

### Condensation dyes

These are produced by condensation of nitro compounds with amines. Alkaline condensation of dinitrostilbene disulphonic acid with amino azo



### 12.6 Tetrakisazo direct dyes.



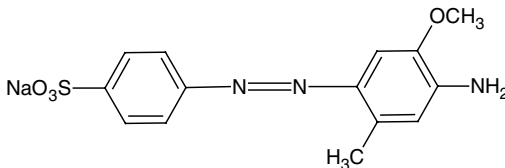
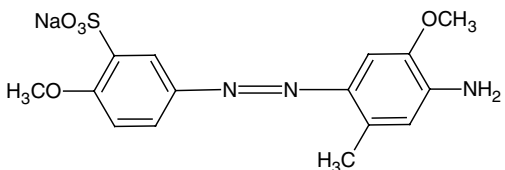
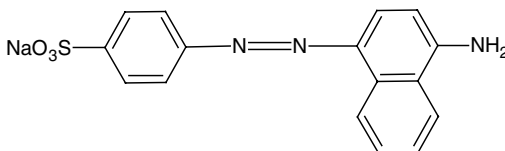
### 12.7 Tetrakisazo direct dye.

compounds produce a number of highly fast substantive dyes with industrial importance, especially in the shades orange, scarlet and brown (Greuly, 1907).

C.I. Direct Orange 39, C.I. 40215 (32) [1325-54-8] is obtained by condensation of 4-aminoazobenzene-4'-sulphonic acid in aqueous sodium hydroxide solution. The main product is the tetrakis azo dye 32. It also contains the corresponding azoxy compounds. No uniform product is obtained, since part of the amino azo compound is consumed as reducing agent. These dyes are generally purified by after-treatment with reducing agents such as glucose or sodium sulphide.

Further examples of condensation dyes obtained by the condensation of aminoazo compounds with 4,4'-dinitrostilbene-2,2'-disulphonic acid are given in Table 12.1.

**Table 12.1** Examples of condensation dyes made from aminoazo compounds and 4,4'-dinitrostilbene-2,2'-disulfonic acid

Aminoazo compounds	Condensation dye	Chemical for after treatment
	C.I. Direct Orange 40 C.I. 40265 [1325-62-8]	Na <sub>2</sub> S
	C.I. Direct Red 76 C.I. 40270 [1325-63-9]	Glucose
	C.I. Direct Brown 78 C.I. 40290 [1325-65-1]	

### *Direct dyes with a urea bridge*

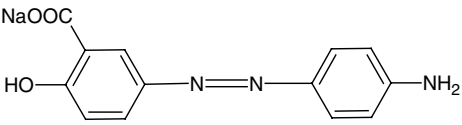
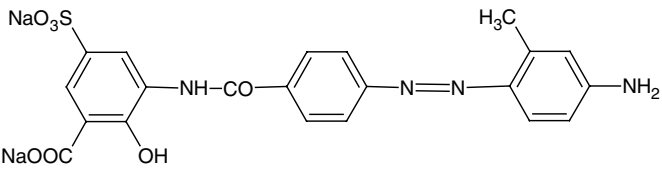
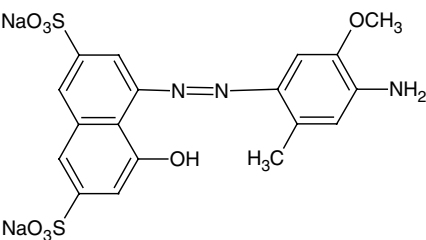
BASF discovered, by the end of the nineteenth century, that the reaction of amino azo dyes with phosgene in an aqueous solution in the presence of base gave valuable symmetrical disazo dyes with urea bridge group. Such dyes can also be prepared from 4,4'-diaminodiphenyl urea derivatives by means of bisdiazotisation and coupling.

C.I. Direct Yellow 50, C.I. 29025 (33) [3214-47-9] is prepared by phosgene treatment of two equivalents of aminoazo dye obtained from diazotised-2-aminonaphthalene-4,8'-disulphonic acid coupled to *m*-toluidine. More examples of such symmetrical direct dyes with urea bridge are shown in Table 12.2.

Red and brown polyazo dyes can also be obtained by treatment of amino disazo dyes and amino trisazo dyes with phosgene. C.I. Direct Red 80, C.I. 35780 [2610-10-8] (34) is obtained by phosgene treatment of the amino disazo dye (35).

Two different aminoazo compounds can be mixed and treated with phosgene to get unsymmetrical diphenyl urea dye. C.I. Direct Yellow 41, C.I. 29005 (36) [8005-53-6] is such an example (Fig. 12.8).

Table 12.2 Amino azo dyes for symmetrical direct dyes with a urea bridge

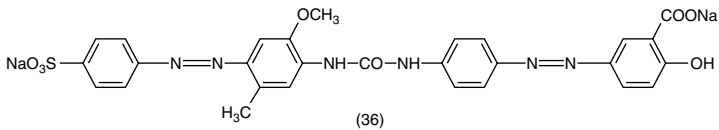
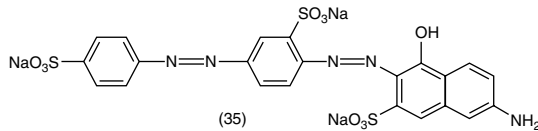
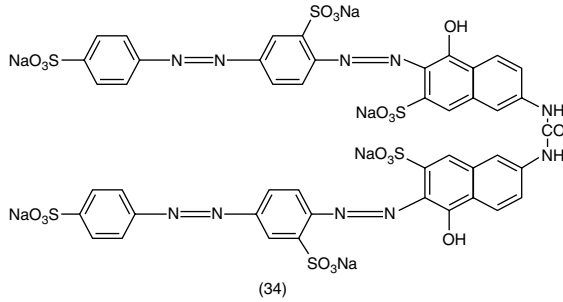
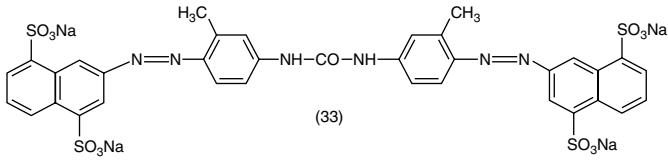
Aminoazo compounds	Condensation dye
	C.I. Direct Orange 40 C.I. 40265 [1325-62-8]
	C.I. Direct Red 76 C.I. 40270 [1325-63-9]
	C.I. Direct Brown 78 C.I. 40290 [1325-65-1]

### Triazinyl direct dyes

Ciba established the principle of linking two or three azo dyes by means of a triazine ring (37). The triazine bridge increases the substantivity of the dyes. This class of dyes is of particular importance in getting green shades through the combination of a blue and yellow component. C.I. Direct Green 26, C.I. 34045 (37) [6388-26-7] is an example which gives a very pure, clear, bluish green with very good fastness properties. In this dye the blue component (H-acid  $\rightarrow$  Cresidine  $\rightarrow$  H-acid) is linked with the triazine ring by means of the amino group of the H-acid; after reduction of the nitro group, the yellow component (p-nitroaniline  $\rightarrow$  salicylic acid) replaces the second chlorine atom of cyanuric chloride, and aniline the third chlorine atom. In another similar dye, C.I. Direct Green 28, C.I. 14155 (38) [6471-09-6], the blue component comes from anthraquinone residue (Fig. 12.9).

### 12.3.2 Direct dyes with after-treatment

Though the wet fastness properties of direct dyes are not outstanding as in the case of reactive dyes, direct dyes continue to hold a large share of the market for inexpensive cellulose and paper dyes. Continuous efforts are being made to improve the fastness properties of direct dyes by after-treatment.



### 12.8 Secondary disazo dyes and dimeric urea containing disazo dyes.

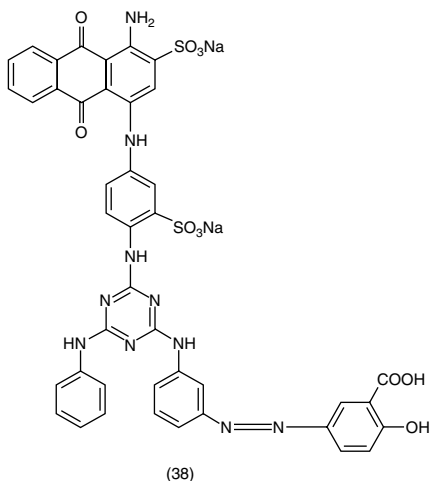
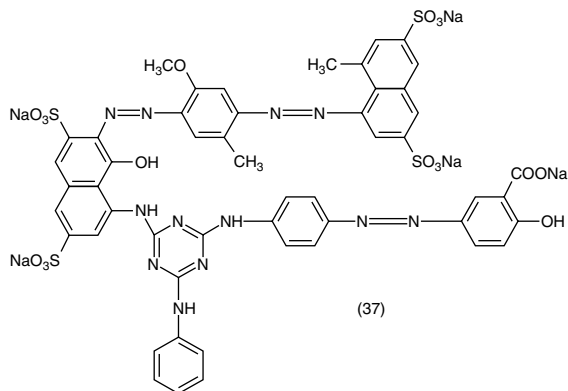
#### *After-treatment with cationic auxiliaries*

On after-treatment of substantive dyeing with organic cationic materials improvements are obtained especially in wet fastness properties as well as fastness to perspiration and cross-dyeing. This process has become recently an important means of enhancing the performance of direct dyed goods.

The cationic auxiliaries precipitate the anionic direct dyes from their aqueous solutions and on the fibre from higher molecular weight, sparingly soluble, salt-like compounds, removal of which from the fibre is made more difficult. This after-treatment is usually accompanied by change of shade.

Quaternary ammonium compounds and cationic formaldehyde condensation resins are used as cationic textile auxiliaries.

When quaternary ammonium compounds are used there exists a possibility of elimination of aliphatic amines, for example in an alkaline medium in the presence of anionic substances or at excessive drying temperatures.



### 12.9 Green direct dyes.

This can cause an unpleasant odour to arise necessitating an after-treatment with acids.

The water-soluble resins are relatively inexpensive, and compared with quaternary ammonium compounds relatively small amounts often suffice to obtain a significant improvement in wet fastness to perspiration.

#### *After-treatment with formaldehyde*

The direct azo dyes containing free amino or hydroxyl groups as terminal groups show improved wet fastness properties on after-treatment of the dyed material with aqueous formaldehyde solution. The free amino functions can also be generated by careful reduction (without destroying the azo groups) or hydrolysis of acylamino groups. During the after-treatment

formaldehyde reacts with the dyes forming methylene bridges between the dye molecules improves the wet fastness leaving the light fastness unaffected.

The materials subjected to this treatment lack storage stability and hence this after-treatment is mainly confined to dark and tertiary shades like browns and blacks. Although the process is simple the ecological factors have kept interest in this process very low.

### *Diazotisation dyes*

Substantive azo dyes bearing one or more diazotisable amino groups make them amenable to further diazotisation and subsequent coupling with a 'developer'. 2-Naphthol can be used as a developer for orange, red, brown, blue and black shades and 1,3-phenylenediamine and 2,4-diaminotoluene for brown, grey and black shades.

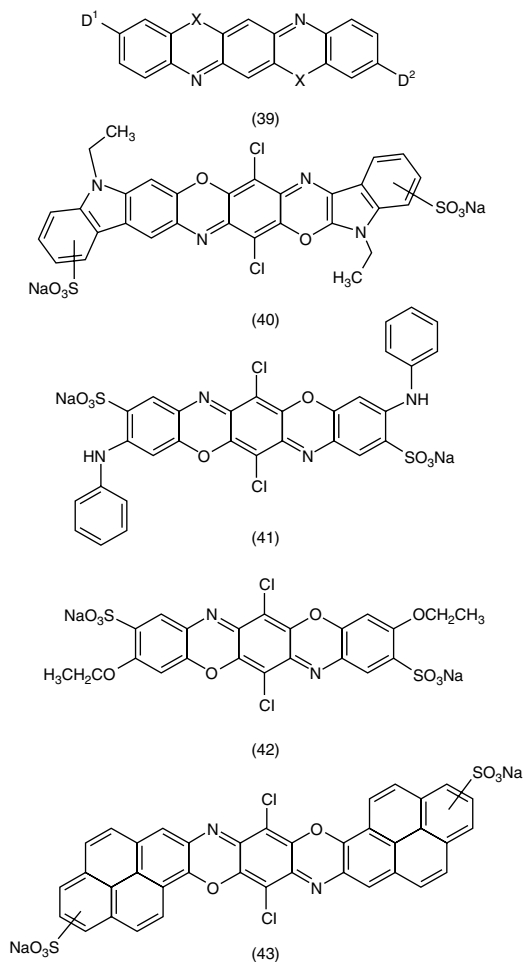
This after-treatment leaves a permanent change in the shade of the material while wet fastness and fastness to perspiration are greatly improved. Light fastness, however, remains unchanged. The amino group originates from the intermediate such as aminonaphthol sulphonic acid, or an amino acylamino naphthol sulphonic acid group or by reduction of a nitro group or hydrolysis of an acylamino group. This after-treatment results in enlargement of the dye molecule without further solubilising groups being added. This process demands more time and careful handling. The importance of this treatment has considerably declined.

### *After-treatment with metal salts*

This treatment results in metal complexation which brings in blocking of solubilising groups, increase in aggregation, decrease in solubility, and an improvement in wash fastness. The light fastness is also generally improved. Catalytic action of traces of heavy metal ions present can cause tendering of the fibre particularly in the presence of detergents containing oxidising agents. This treatment makes the shade duller and flatter.

## **12.4 Bisazine dyes and copper phthalocyanine dyes**

These dyes have the general formula 39 where  $D^1$  and  $D^2$  represent the donor groups. The chromophore can be visualised as 1,4-didonor-2,5-diacceptor substituted benzene. The groups  $D^1$  and  $D^2$  are not really required and are lacking in a large number of important dyes. The bisazine dyes include the fluoridine dyes ( $X = N$ ), the dioxazine dyes ( $X = O$ ) and the dithiazine dyes. Among these, the dioxazine dyes have the greatest industrial importance. Unsulphonated compounds are important pigments.



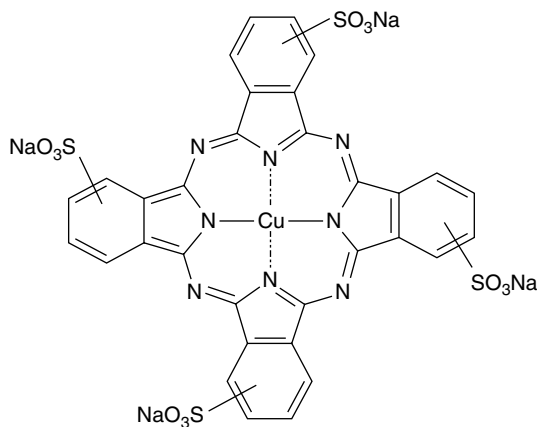
### 12.10 Triphenodioxazine direct dyes.

Dioxazine dyes are prepared by the reaction of benzoquinone derivatives, in particular tetrachloro benzoquinone (chloranil) with aromatic amines in presence of an acid binding agent, followed by oxidative cyclisations.

Sirius Light Blue FFRL, or Remastral Blue FFRRL, C.I. 51320 [1324-58-9] (94) is prepared by condensation of chloranil and 3-amino-*N*-ethyl carbazole followed by sulphonation. Other examples are Sirius Light Blue FF2GL, or Remastral Blue FF2GL, C.I. 51300 [30282-46-3] (42) and Sirius Light Violet FRL, or Remastral Violet FrL, C.I. 51325 [1324-43-2] (43).

Partially sulphonated derivatives of copper phthalocyanine are commercially important brilliant turquoise blue acid and direct dyes (Figs. 12.10 and 12.11).





(44)

12.11 Copper phthalocyanine-based direct dye.

## 12.5 Future trends

The advent of reactive dyes has made brought progress of research in direct dyes almost to a halt. However, there seem to be interest in the developments of substitutes for carcinogenic diamines as well as toxicity of direct dyes. None of the innovative diamines embodied in the published literature has taken the limelight. Improvement in wash fastness, light fastness and other application characteristics need yet to be addressed.

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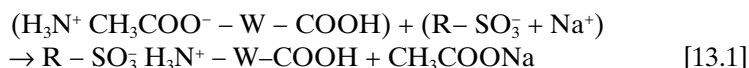
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Jalandhar, India

**Abstract:** Metal-complex dyes are synthesised through coordination of bi- or polyvalent transition metal ions with selective acid dyes. They are mainly applied to wool, silk and nylon to achieve better wash fastness for dyed fabrics, compared to those obtained with the parent acid dye. These dyes may be produced on the substrate, during dyeing, through a one- or two-step process, which is known as mordant dye. Alternatively the metal is chelated in the dye structure by the manufacturer before application, which is called premetallised dye. Overall increase in the size of the acid dye molecules after coordination with metal is at the root of improved wash fastness. The extent of exhaustion, diffusion and levelling through migration, is utilised to promote build-up of shade. Chromium salt, the most commonly used mordant, increases waste-water load. This has necessitated development of eco-friendly formazan and other dyes through complex formation with iron and aluminium. In spite of this, metal-complexed dyes, especially 1:2 chromium premetallised dyes, are commercially important to produce bright, wash-fast shades on natural protein and polyamide fibres without the risk of over-dyeing and degradation of fibre.

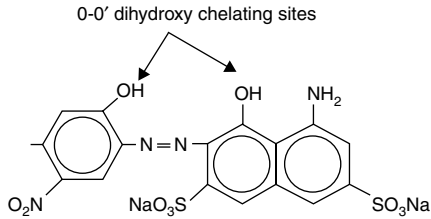
**Key words:** acid dye, metal, metal-complex dye, mordant dye, premetallised dye.

### 13.1 Introduction

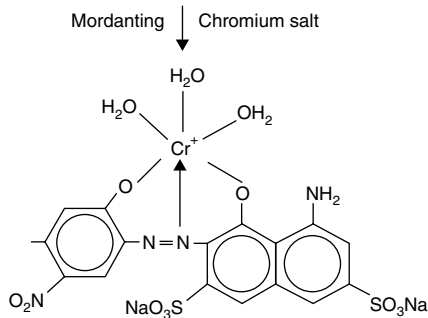
Overall poor wash fastness of acid dyes, specifically strong acid dyes on protein and polyamide fibres, is due to the smaller size of dye molecules which establish a weaker ionic attachment with the fibre.



A higher concentration of acid in a bath (i.e. the lower the pH), combined with a longer dyeing time, will cause the formation of more protonated amino groups. This will lead to a higher rate of dye-fibre bond formation. However, the ionic linkage established is not strong; the dye molecules can be easily detached and reformed under favourable circumstances. This in



Cl Mordant Green 17, C.I. 17225 (Colour Index, 1987)



13.1 Formation of metal-complex dyes.

turn causes migration of dye, which is favoured by solubility of acid dyes in the bath.

During domestic washing, the stripping out of colour and staining of adjacent garments poses a problem, which can become severe with levelling acid dyes. However, this can be improved, though not by a significant amount, with the use of milling and super-milling dyes, since these are larger dye molecules. This migration of acid dye can be reduced or halted, if the dye structure is made significantly large. Metal-complex dyes are selective acid dyes possessing chelating sites to coordinate with metal atoms to develop bigger dye-metal complexes through coordinate and covalent bond formation (Fig. 13.1).

These dyes are often used for dyeing of wool, silk and nylon to produce fast shades (Shenai, 2002). When produced on a substrate, the dye-metal complex is called mordant dye and, if manufactured before dyeing, is called premetallised dye.

## 13.2 General properties

Metal-complex dyes have low water solubility; the solubility decreases from 1:1 metal-complex type to 1:2 complex type (see Section 13.6); most are of

monoazo type and are derived through complexation of selective metals with acid dyes possessing o-o' chelating sites such as  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ , etc. The electron donating ligand or ion combines with a transition metal ion to form the complex. In order to form a complex, there must be at least two ligands in the dye structure. However,  $-\text{tridentate}$  or  $-\text{tetradentate}$  ligands in the parent acid dye structure occupy three or four coordination sites of the transition metal ion. The combination of ligands with metal ions depends on the coordination number of the metal. For instance, bivalent  $\text{Cu}^{2+}$  ion, possessing coordination number four, can be complexed with two bidentate ligands in an acid dye or a trivalent or a tetravalent one. When coordination of  $\text{Cu}^{2+}$  ion occurs with a tridentate ligand, the fourth coordination site is generally occupied by a solvent molecule. Trivalent chromium ( $\text{Cr}^{3+}$ ) or cobalt ( $\text{Co}^{3+}$ ) have coordination number six and hence can easily form 1:1 and 1:2 metal-complex dyes. In 1:1 complexes, three coordination sites are occupied by trivalent metal, whereas the remaining three coordination sites are occupied by solvents, like water. Due to the better stability of 1:1 complexes in strong acidic conditions ( $\text{pH} < 4.0$ ), these dyes are preferably applied to textiles at a pH lower than 4.0. 1:2 complexes, on the other hand, are more stable in weak acidic conditions, and are therefore applied in a weak acidic or neutral bath ( $\sim\text{pH} 5.0\text{--}7.0$ ). Preparation of a 1:1 complex is possible at lower temperatures, but 1:2 complexes are synthesised only at an elevated temperature, thus limiting production by manufacturers.

Metal-complex dyes are not necessarily derivatives of acid dyes; reactive-, direct- and metal-complexed vat dyes are also well developed, though they are not widely used for the dyeing of protein fibres. Even copper, chromium, cobalt and nickel complexed reactive dyes, which are used to produce turquoise blue and brilliant green, are unmatched with other dyes. However, eco-concern has forced dye manufacturers to introduce phthalocyanine groups in place of metals with comparable results (Benny and Janakiraman, 1999).

Metals often used to form a complex are copper, cobalt, nickel and chromium. Chromium complexed dyes are exclusively used on substrates requiring high light and wash fastness qualities compared to those produced by other dyes (Hannemann, 2001; Kocaokutgen and Ozknal, 2004). All these four metals are soluble in perspiration at varying extents, showing a negative impact on the human body in humid conditions.

1:1 premetallised dyes can cause moderate dye uptake on wool and silk, but they can offer low saturation values on nylon 6,6, and exhibit low to moderate coverage of fibre irregularities and poor compatibility in mixtures. The strong pH required for dyeing may result in over dyeing through dye attachment at peptide linkages ( $\text{CO-NH}$ ) of the fibres. In most dyeing situations with these dyes, pH should be maintained higher than 2.7 (the iso-electric point below which the rate of dyeing increases rapidly), preferably nearer to pH 4.0. In contrast, 1:2 premetallised dyes display high build-up on wool, silk and nylon

fabrics, and exhibit high compatibility in mixtures (Sekar, 2000); the weak pH of the bath during the dyeing process does not assist over dyeing.

1:2 complexes based on 5-methyl substituted groups of o-o' dihydroxy azo dyes with chromium or cobalt, offer excellent exhaustion on nylon along with outstanding fastness properties (Kocaokutgen *et al.*, 1998). Other applications of metal-complex dyes include the production of writing ink, paint, printing ink, ink-jet dyes, toners for photocopiers and photoconductors for laser printers as well as the dyeing of leather, fur and hair.

### 13.3 Chemistry of dyes

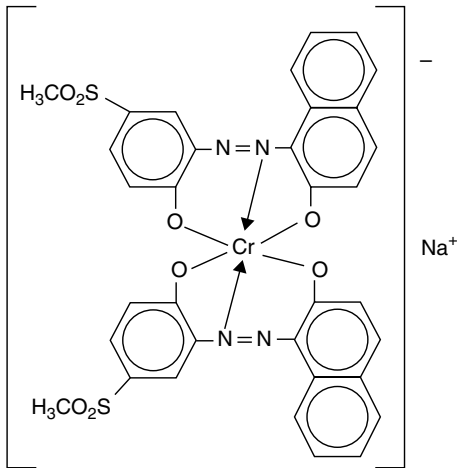
Acid dyes possessing chelating sites with identical or dissimilar functional groups, such as hydroxyl or carboxyl at o-o' locations with respect to azo chromophore, are capable of producing metal-complex dyes. The chemical groups in these locations may be either of 2,2'-dihydroxy, 2-carboxy-2'-hydroxy or 2-amino-2'-hydroxy; whereas the complex forming ligands are trivalent and form three bonds to a transition metal ion.

The nomenclature of acid dye-metal product is more appropriately referred to as 'metal-complexed acid dyes'. The complex formation occurs through substitution of two protons by the metal ion, one each from two substitutive groups for 1:1 complex dye.

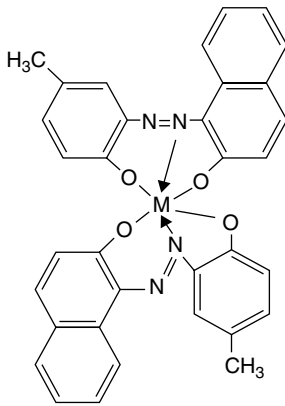
1:1 metal-complex dyes of copper, nickel, cobalt or zinc with 5-cyano-6-methyl-2-2'-bipyridine have been found to be highly effective on protein fibres (Matsui *et al.*, 1992).

Monoazo based 1:2 metal-complex dyes can be categorised into three main types: nonsulphonated, monosulphonated and disulphonated (Szymczyk *et al.*, 1998). The so-called green or eco-friendly dyes of natural origin are based on iron-complexed dyes. Harmful metals such as cobalt, nickel, copper and chromium, when used for complex formation, may be extracted with artificial saliva or acid perspiration solution during corresponding fastness evaluation. One important class for iron-complex formation is o-o'-dihydroxy azo dyes. The coupling component preferred for preparation of azo dye is 1-naphthol, 2-naphthol and arylides of acetoacetic acid. This acid limits the range of shades available, developing only yellow-brown to olive-brown, violet-brown and black-brown shades (Sekar, 1999).

Azomethine dyes are complexes of nickel, cobalt and copper with 2-pyridylmethylene-1-amino-2-naphthol. Coordination occurs through nitrogen of the pyridine ring and the azomethine group, as well as through the oxygen atom of the hydroxyl group (Sekar, 2003). Affinity of all these complexes are remarkably good for protein and polyamide fibres with excellent wash and light fastness. The degree of exhaustion increases from nickel to cobalt and from cobalt to copper, which further increases proportionately with an increase in dyeing temperature (Koprivanac *et al.*, 1993).



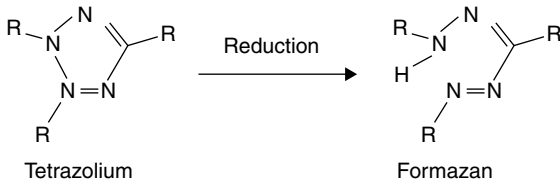
13.2 Irgalan dyes.



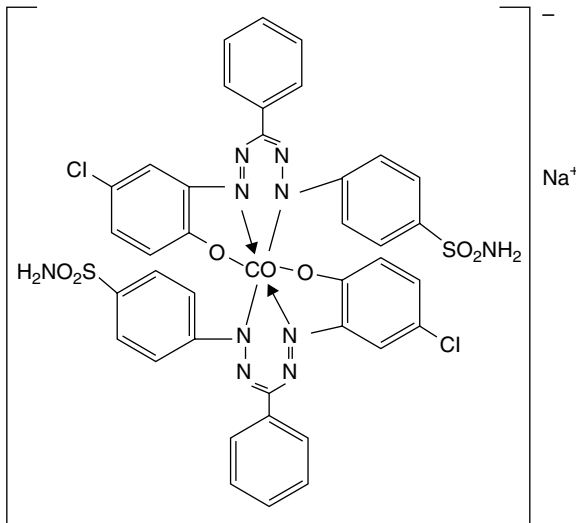
13.3 Formation of 5-methyl substituted metal-complex dye.

During complex formation of chromium salt with acid dye, out of six coordination sites of chromium, three are used by the dye and the remaining three by water molecules in acidic neutral pH or hydroxyl ions in alkaline pH (Race *et al.*, 1946). To improve water solubility of 1:2 dyes, a new series has been developed by introducing non-hydrophilic methylsulphonyl, sulphonamide or acetyl amino groups without affecting dyeing and fastness properties. These substituents are not acidic and the solubilising effect is due to covalent bond formation between water and sulphonyl oxygen atoms or C=O groups, known as Irgalan dyes (GY). These are shown in Fig. 13.2 and the formation of 5-methyl substituted metal-complex dye in Fig. 13.3 (Schetty, 1955; Zollinger, 1961).





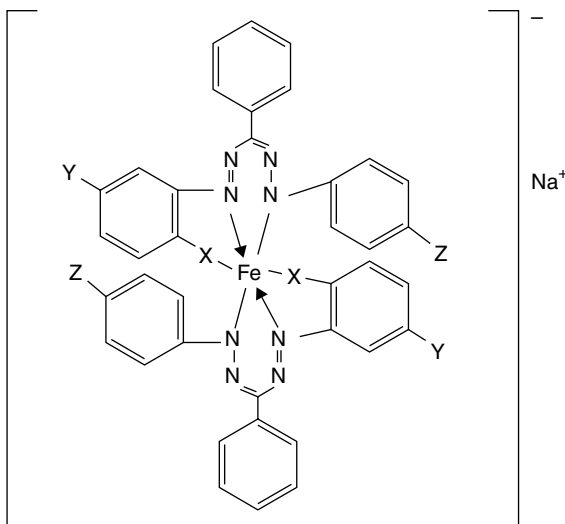
#### 13.4 Synthesis of formazan.



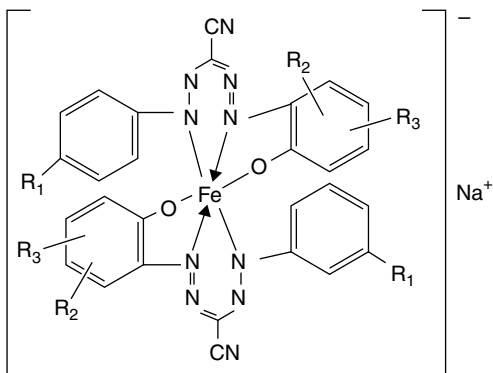
#### 13.5 Cobalt-complexed formazan dyes.

Formazans, obtained through reduction of water-soluble colourless tetrazolium salts (Fig. 13.4), are capable of producing very fast and intense reactions with several metal ions to produce symmetric and unsymmetric 1:2 iron-complexed formazan dyes, without having any adverse effect on dye stability and excellent light fastness. The affinity for nylon is also good, with a wider hue range. One such structure of cobalt-complexed formazan is shown in Fig. 13.5 (Sekar, 2001b), with C.I. generic name Acid Black 180 and C.I. number 13710.

Formazan dyes complexed with Co(II), Cr(III) and Cu(II) are widely in use in industry, but environmentally hazardous; this has necessitated the development of several iron(II) complexed formazan dyes. Synthesis of iron-complexed formazan dyes are mainly based on diazotisation of *o*-aminophenol derivative or anthranilic acid and coupling with either of benzaldehyde phenylhydrazones, benzaldehyde phenylhydrazone-4-sulphonamide, benzaldehyde phenylhydrazone-4-sulphonic acid succeeded by complexation with iron(II) sulphate (Freeman *et al.*, 1997; Sokolowska *et al.*, 1996). The general structure of such dyes is represented in Fig. 13.6. Recent synthesis



13.6 General structure of iron-complexed formazan dyes.

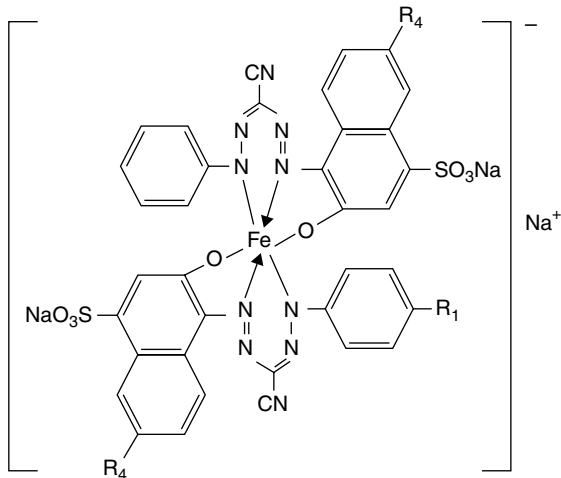


13.7 Iron-complexed formazan dyes (type-1).

of formazan 1:2 iron-complexed dyes are based on 1,5-diaryl-3-cyanofor-mazanes (Figs. 13.7 and 13.8) with a higher affinity for polyamide fibres and a wider shade range (Szymczyk *et al.*, 1999). Recently, such iron-complexed azo dyes, possessing trifluoroacetamido and mesylamido groups, have also been synthesised (Szymczyk *et al.*, 2007). After-chrome dyes have also been developed to be complexed with iron (Czajkowski and Szymczyk 1998).

### 13.4 Classification and nomenclature

There are two types of metal-complexed acid dyes: mordant and premetal-lised. The reaction of the metal (such as chromium) with a coordinating acid



13.8 Iron-complexed formazan dyes (type-2).

dye produces dull shades. This is the case for both types of acid dye, though the dullness is more extreme with mordant dyes. A shift in  $\lambda_{\max}$  is observed during this reaction, due to the bathochromic effect, causing a change in the final hue of the metal (Burkinshaw, 1992a).

#### 13.4.1 Mordant dye

Mordant dyes are produced when the dye can only react with metal on the substrate once, but in varying sequences, for example when dyeing with a selective acid dye is preceded or succeeded by pre-treatment with a metal salt, or when a concurrent treatment with dye and metal salt is used. At most, one molecule of dye can be reacted with one metal ion by the dyer. In mordant acid dyes, the metal acts as an acceptor to an electron donor to form a coordinate bond.

#### 13.4.2 Premetallised dye

A metal atom is reacted with one or two dye molecules by the manufacturer during synthesis to develop premetallised dyes. Reaction of one atom of metal with one or two molecules of dyes are known as 1:1 and 1:2 metal-complexed acid dyes, respectively.

It must be kept in mind that all mordant dyes are 1:1 complex, but the latter is free from any excess metal and is an environmentally safe product. Dyeing with mordant dyes is generally a two-stage or two-bath process, whilst dyeing with 1:1 complexed dye is a single-bath process at low pH. Application parameters of 1:1 and 1:2 premetallised dyes are similar to those of levelling

and milling acid dyes, though type 1:2 has been favoured due to superior all-round fastness and mild acidic dyeing conditions (Burkinshaw, 1992a).

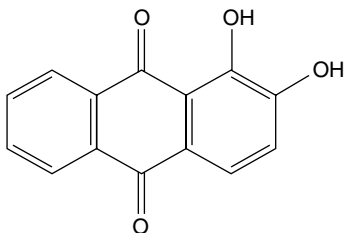
### 13.5 Mordant dyes

A mordant is a simple chemical which possesses affinity for both fibre and dye. If a dye has less or no affinity for fibre, the mordant previously applied improves affinity of that dye and makes a dye–mordant–fibre complex. Mordants are metal salts and are electrically cationic. In contrast, all acid dyes are anionic in nature, and their affinity is increased a large amount when mordant is applied on the fibre before application of the dye. Various natural dyes, such as logwood black or madder, are also used for dyeing wool with the help of mordants such as alum, chrome, iron and tin salts. Brighter colours and better fixation can only be obtained by pre-mordanting. Some substantive or non-mordant dyes, such as turmeric, berberis, doli, annato and henna, contain tannin in the colouring matter itself as a natural mordant, and can produce fast colours when applied at the boil.

All mordant dyes are acid dyes, but the reverse is not true. In simpler techniques, chromium salts are invariably used for complex formation, the reactions are carried out during dyeing to obtain the dye-metal complex. These are often referred to as chrome dyes. Chromium salts act as efficient mordants, e.g.  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Mordant dyes do not only promote dye–metal complex formation to improve fastness, but they also enhance acid dye uptake due to the cationic nature of chromium salts when applied to wool before dyeing (Gills, 1944). These mordant dyeing methods are useful tools for cottage industries to dye wool with superior wash fastness. A single mordant with different mordant dyes, or vice versa, can produce a wide range of hues.

Mordant dyes are classified chemically as azo, anthraquinone, oxazine, xanthene, triphenyl methane, nitroso and thiazine types, in which only azo dyes have a good spectral colour range and are subsequently more prominent (Shenai, 1987). Alizarin (Fig. 13.9), chemically 1,2 dihydroxyanthraquinone, C.I. Mordant Red 11, C.I. 58000 (SDC, 1987), is one of the important



13.9 Alizarin.

anthraquinone mordant dyes. It is used with various mordants to develop different hues, for example aluminium (red), ferrous iron (deep violet), ferric iron (brownish black), stannous tin (reddish violet), stannic tin (violet) and chromium (brownish violet). Alizarin is not an acid dye. It has the chelating sites required for complex formation with mordants, frequently derived from madder (Allen, 1971).

Mordanting can take place before, after or concurrently with the dyeing process. Depending on the stage at which mordants are used, chrome dyeing methods are classified as (i) onchrome, (ii) metachrome and (iii) after-chrome. Chromium salts are exclusively used as a mordant in all these processes, whereas other mordants derived from copper, cobalt, nickel and aluminium are often used with the latest iron-based mordants.

### 13.5.1 Onchrome

Chroming of fibre is carried out first, followed by dyeing with a selective mordant dye. Chromium in a higher valency state is applied to the woolen material, by treating in  $K_2Cr_2O_7$  solution either in a neutral condition known as 'sweet chrome' or in an acidic condition known as the 'sour chrome' method. The reduced chrome method is used for dyes that are susceptible to oxidising agents. In the 'sweet chrome' method, wool is treated with  $K_2Cr_2O_7$  solution (2%) in neutral pH at 60°C for 30 min. Chromium in a higher valency state is absorbed by the wool, forming a wool–chromium complex consuming only half the amount of chromium. In the 'sour chrome' process,  $K_2Cr_2O_7$  (1–2%) is applied with  $H_2SO_4$  (1%) at 60°C for 30 min, when all the chromium is absorbed by wool. In both these cases, chroming is succeeded by dyeing with selective mordant dyes.

The 'reduced chrome' method is especially useful for dyes susceptible to oxidation. The pre-treatment is carried out using  $K_2Cr_2O_7$  (2%), lactic acid (3–4%) at 60°C for 15–20 min.

All of the 'on chrome' methods are two-bath processes; this is expensive and usually only one batch of material can be chromed per process. The methods are also only suitable for light and medium shades. In contrast, matching of colour is relatively easy; regular building of shade occurs on tone with little change in shade during dyeing.

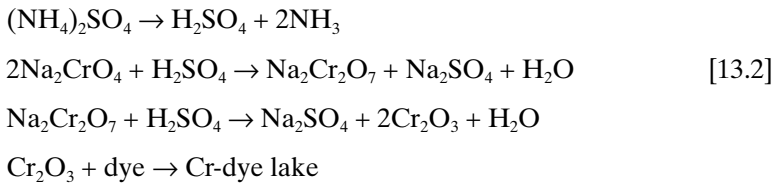
Pre-mordanting increases dye uptake substantially because of electrostatic interaction between the mordant and the dye.

### 13.5.2 Metachrome

Milling and super-milling acid dyes with chelating sites are most suitable for the metachrome process; they exhaust well at a pH of 6.0–8.5. In this

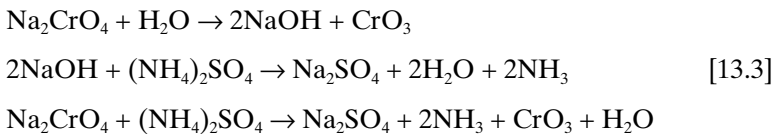
single-bath process, the dye and the mordant are simultaneously applied in the same bath. In spite of being electrically opposite in nature, the dye and the mordant do not react initially, rather both are exhausted on the substrate after which the dye-mordant reaction occurs *in situ* under favourable conditions to develop the hue. If conditions are not maintained properly during exhaustion, the dye and the mordant react in the bath and the metal-complexed dye is precipitated from the dyebath.

Chromium is deposited on, or combines with, the fibre, followed by reduction of  $\text{CrO}_3$  to  $\text{Cr}_2\text{O}_3$  at the boil. At the same time, dye combines with the wool in the same way as with a milling acid dye. The dye and the reduced chromium then combine with fibre to form a dye–chromium–wool complex. It is likely that all three reactions occur simultaneously in bath (Shenai, 1987).



The chances of the formation of another metal–dye–fibre complex, rather than with chromium, arising from the presence of other metals that may be present in the supply water used for dyeing is prevented by chromates which form a protective oxide film on the surface of other metals and do not allow them to take part in reaction.

A dyebath usually contains dye,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{CrO}_4$  (sodium chromate) or  $\text{Na}_2\text{Cr}_2\text{O}_7$ .  $(\text{NH}_4)_2\text{SO}_4$  promotes deposition of  $\text{CrO}_3$  on the wool without damaging it and generates a pH around 6.0–8.5. Due to generation of  $\text{NH}_4\text{OH}$ , the bath is likely to become alkaline with time, in a closed dyeing machine.



Pre-treated wool is treated with  $\text{Na}_2\text{Cr}_2\text{O}_7$  (2–5%), Glauber's salt (5–10%) and surfactant (0.5 g/L) at 40–50°C for 20 min. Dissolved dye is then added, and the temperature is raised to 90–95°C over a period of 45 min. The treatment is continued at this temperature for further 60–90 min; exhaustion may be enhanced by applying 0.5–1% of  $\text{CH}_3\text{COOH}$  (40%) or half the amount of  $\text{HCOOH}$  (85%), preferably 30 min before dyeing is completed.  $\text{CrO}_3$  is

reduced to  $\text{Cr}_2\text{O}_3$  by the wool during this process.  $(\text{NH}_4)_2\text{SO}_4$  may be substituted with  $\text{CH}_3\text{COONH}_4$  when using dyes known to cause uneven dyeing.

The 'metachrome' process is a single-bath process; it is simple to apply with a higher rate of production/time. Shade matching is easier because the final shade is produced during dyeing. Chromium does not form a complex with the dye in chromate form, permitting the application of sodium chromate and dye from the same bath; pH of the dyebath is maintained at around 6.0–8.5 for maximum conversion of dichromate to chromate (Peters, 1975). The dulling of shade due to presence of iron or copper does not occur, as it often does in other chrome dyeing methods. One prerequisite is that only dyes which do not react with hexavalent chromium ( $\text{Cr}^{6+}$ ) can be used in this method. In spite of all this, the range of shade is limited, as only a few dyes are suitable for this method and unlevel dyeing cannot be rectified. In deep shades, the dye is prone to poor rubbing fastness due to precipitation of the dye onto the fibre surface. Due to relatively higher pH of the bath, exhaustion remains incomplete, especially with deeper shades; blacks, navy blue and other deep shades are seldom produced in this method (Trotman, 1994).

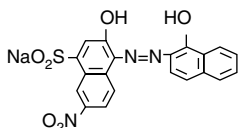
### 13.5.3 After-chrome

Chrome dyes are first applied to wool in the presence of an acid, followed by the addition of  $\text{K}_2\text{Cr}_2\text{O}_7$  (1–2%) in the same or a separate bath at 60–80°C. The results of this process show superior fastness to milling and potting (Hannemann, 2001). Shade matching is not easy and any change in shade can be difficult to rectify. However, the concentration of dichromate required is remarkably less than other mordant dyeing methods. This has led to this method becoming more popular, although the dye uptake is lower compared to that obtained using the onchrome method.

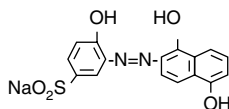
All chrome dyeing methods suffer from the increased stiffness of the dyed fibre, due to precipitation of a part of the complex at the interstices as well as the formation of the complex on the surface of the substrate. The formation of dull shades with change in hue, in comparison to that produced with parent acid dye, poses problems in dyeing wool. The reproduction of hue and shade becomes difficult, and partial tendering of the wool keratin occurs due to prolonged dyebath treatment (Burkinshaw, 1992a). The Colour Index specification and chemical structure of specific mordant dyes are illustrated in Fig. 13.10 (SDC, 1987). All dyebaths are mostly two-bath or two-stage processes. Dyes suitable for various chrome methods have been listed elsewhere (Shenai, 1987).

## 13.6 Premetallised dyes

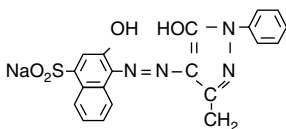
Selective acid dyes are complexed with copper, chromium, cobalt or nickel at specific proportions to develop these dyes. The reaction of one metal ion



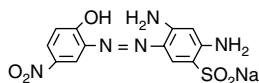
Eriochrome Black T (Bluish Black)  
C.I. Mordant Black 11, C.I. 14645



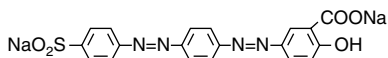
Atlantichrome Black PV (Black)  
C.I. Mordant Black 9, C.I. 16500



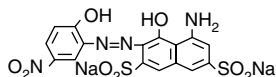
Acid Chrome Bordeaux B (Bluish Red)  
C.I. Mordant Red 7, C.I. 18760



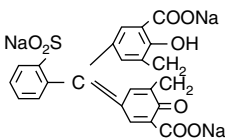
Acid Chrome Brown RH (Yellowish Brown)  
C.I. Mordant Brown 33, C.I. 13250



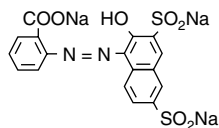
Acid Chrome Orange G (Reddish orange)  
C.I. Mordant Orange 6, C.I. 26520



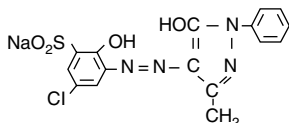
Acid Chrome Green G (Bluish Green)  
C.I. Mordant Green 17, C.I. 17225



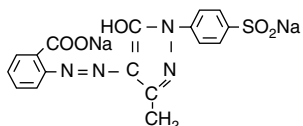
Chrome Cyanine RLA (Bright Reddish Blue)  
C.I. Mordant Blue 3, C.I. 43820



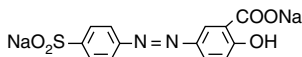
Acid Chrome Red B (Bluish Red)  
C.I. Mordant Red 9, C.I. 16105



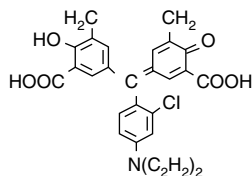
Chrome Fast Red GW (Bright Red)  
C.I. Mordant Red 19, C.I. 18735



Acid Chrome Yellow FR (Reddish Yellow)  
C.I. Mordant Yellow 8, C.I. 18821



Chromefast Yellow 2G (Greenish Yellow)  
C.I. Mordant Yellow 10, C.I. 14010



Eriochrome Violet B (Bluish Violet)  
C.I. Mordant Violet 28, C.I. 43570

### 13.10 C.I. specification and chemical structure of some mordant dyes.

with one molecule of dye produces 1:1 metal-complex dyes, whereas the reaction of one metal ion with two molecules of dye produces 1:2 metal-complex dyes. All of the valences of a metal are not coordinated with only one dye molecule, and so unsaturation exists in the 1:1 complex. This may



lead to the formation of 1:2 unsymmetrical complexes with two different dye molecules.

### 13.6.1 Premetallised dye – 1:1 type

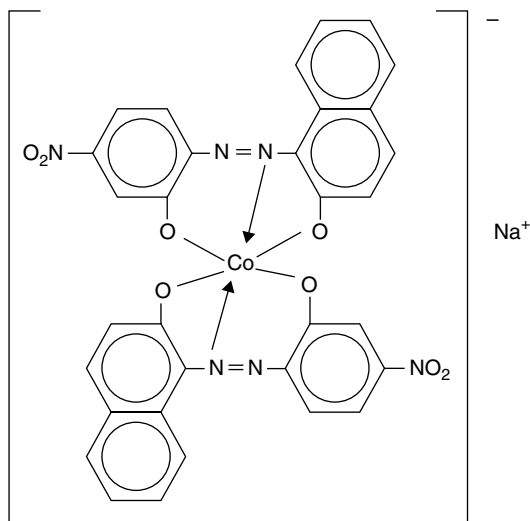
Premetallised dyes are mainly synthesised from *o*-*o'*-dihydroxyazo, *o*-carboxy *o'*-hydroxyazo, *o*-amino *o'*-hydroxyazo, *o*-hydroxy, and *o'*-methoxyazo types of acid dyes (Allen, 1971). Neolan (Ciba) and Palatine (BASF) dyes are 1:1 metal-complex dyes, produced from the reaction of chromium salts with *o*-*o'*-dihydroxy azo dyes. These dyes are applied using a strong acidic bath ( $\text{H}_2\text{SO}_4$ , 8%). Due to the absence of the dulling effect caused by a wool-chromium complex, shades can be brighter and matching is simpler compared to mordant dyes. All light to heavy shades can easily be produced with these dyes. Light fastness is parallel to mordant dyes, with a slight deterioration in wash fastness. Dyes are water soluble because of  $-\text{SO}_3\text{H}$  groups in the dye structure. To give the true shade and tone, dyeing must be undertaken at a boiling temperature. Cycolan (Geigy), Ultralan (ICI), Chromacyl (Du Pont), Inochrome (Francolor) and Vitrolan (Clariant) were some of the commercial dyes that used to be available; however, these have since been withdrawn from production.

The addition of cationic levelling agents in the dyebath will reduce the concentration of acid required for dye exhaustion. Examples of these levelling agents are Palatine fast salt O and Neolan Salt II, which are fatty alcohol-ethylene oxide condensates, having the general formula  $\text{CH}_3-[\text{CH}_2]_x-\text{O}-[\text{CH}_2-\text{CH}_2\text{O}]-\text{H}$ . Levelling agents form a loose complex with the dye as these are of an opposite electrical nature. The complex is absorbed by the fibre and as the dyebath temperature reaches the boiling temperature, the complex breaks down to release the levelling agents, which allows diffusion of the dye into the fibre (Shenai, 1987). Thorough washing and neutralisation at the end of dyeing are essential to remove residual acid from the fibre.

Dyes exhibit lower exhaustion when applied at neutral pH compared to the conventional low pH application conditions, with consequently poor rubbing, milling and light fastness.

### 13.6.2 Premetallised dye – 1:2 type

Problems associated with dyeing using 1:1 dyes led to the introduction of 1:2 metal-complex dyes. The specifications for these dyes were that they should carry a negative charge and any residual valency of the metal atoms must be fully or nearly satisfied. Also the solubilising groups should be made less hydrophilic, by introducing sulphonamide groups in place of  $-\text{SO}_3\text{H}$ . The complex should retain no hydrophilic groups or a minimum number of them, and all dyes in the range should have identical exhaustion properties.



13.11 Formation of 1:2 premetallised dye (cobalt-complex).

1:2 metal-complex dyes are applied from mildly acidic or neutral dyebaths. The degree of exhaustion and wash fastness are a function of the molecular weight of the dye. A dye with a molecular weight of 600 will exhibit good exhaustion and wash fastness properties, and the inclusion of water solubilising groups, such as  $-\text{SO}_2-\text{CH}_3$ ,  $-\text{NHCOCH}_3$  and  $-\text{SO}_3-\text{CH}_2$  can also improve the dye solubility in the dyebath.

1:2 metal-complex dyes are simple to apply and have relatively short dyeing times depending on depth of shade. They have good levelling and fastness properties, and they can also make batch to batch reproduction easier. An example of a 1:2 cobalt-complex is depicted in Fig. 13.11 (Allen, 1971). These dyes possess little migrating power, necessitating careful control over the pH and a slow rate of heating, since the rate of dyeing is rapid at temperatures just below the boil. Dyeing at a pH around 6.5 at the boil produces level dyeing with maximum dye uptake. To increase the rate of dyeing towards the end of the process, the pH can be lowered down to 4.0. Due to the poor migrating power of these dyes, agitation of the dyebath is essential from the start of the dyeing process, for an even distribution of dye. Shade correction or dye addition can be conducted at the boil after adding  $-\text{NH}_3$  to raise the pH, in order to slow down the rate of exhaustion of the dye addition. Salt alone is not capable of showing any retarding or levelling action, but in the presence of levelling agents, such as Lyogen SMK (Sandoz), salt levelling is pronounced.

Blends such as nylon-cotton, wool-cotton and silk-cotton can also be successfully dyed with 1:2 metal-complex dyes. In order to achieve successful results, the blend requires a pre-treatment with a cationic fixing agent such

as Matexil FC-ER (a cationic polymer based on dimethyldiallyl ammonium chloride) for the cotton portion of the blend, followed by dyeing with the metal-complex dye. The pre-treated fabrics showed excellent dye uptake with respect to their untreated counterparts. The blended fabrics that had been pre-treated showed only a slight difference in colour, or in depth of shade, between the cotton portion and the polyamide portion. Light and wash fastness of the dyed fabric was moderate, depending on the pre-treatment applied (Blackburn *et al.*, 2000).

### 13.7 Fastness of dyed fabrics

Wash fastness is reasonably good, in spite of the poor diffusion caused by the large structure of the dye. However wash fastness may be improved to a good level through the use of back tanning, especially for medium or deep shades (Sekar, 2001a). This is conducted by either post-treatment of dyed fabrics with a syntan such as Fixogene AXF, or the cationic agent Fixogene CXF (Burkinshaw and Son, 2001; Burkinshaw *et al.*, 2001). Wash fastness of conventional and micro fibre nylon 6,6 dyed with 1:2 metal-complex dye is somewhat better than that with the parent acid dye. After-treatment with a syntan, e.g. Fixogene AXE, can further improve wash fastness and a sequential application of Fixogene AC syntan, or cationic reagent to the syntanned dyeing, results in further improvement (Blackburn and Burkinshaw, 1999). Light fastness of all metal-complex dyes is reasonably good. Due to the chances of solubilisation in perspiration, related fastness seems to be poor. Rubbing fastness is good for dry rubbing, but only moderate to poor for wet rubbing.

### 13.8 The problem of waste water

Although wool is dyeable with direct, reactive, acid and metal-complexed dyes, almost 70% are dyed using metal-complex dyes, preferably with chromium complexes. Chromium exists as free ions in two oxidation states, III and VI, or in a complexed form (Thomas *et al.*, 1992; Welham, 1986). The hexavalent form of chromium is highly toxic and so total chromium content in waste water is bifurcated from the hexavalent form (Duffield *et al.*, 1991). Few of the reactive dyes used in wool dyeing are also complexed with either copper or nickel. Chelex resins (BioRad Lab) based on imidodiacetic acid groups with styrene divinyl benzene co-polymer form stable chelates with a variety of transition metals, and they are widely used to remove trace metal ions from waste water. Elimination of metal was found to be inversely proportionate to the stability of the complex; the higher the stability the poorer the elimination. The azo ligands in chromium complexed acid dyes are not as strongly bound to the metal as the ligands are in copper and

nickel complexed reactive dyes. Overall, removal is quite low for copper and nickel complexed reactive dyes (~7–8%), but is quite high for chromium complexed acid dyes (~12–67%) indicating ease in removal of chromium complexed dyes (Hill *et al.*, 1993).

When using mordant dyes, unexhausted dyes can react within the dye-bath and are precipitated. These cannot be recovered and reused. In contrast, premetallised dyes are safe products and unused dye can be separated out through reverse osmosis and recycled (Diaper *et al.*, 1996).

The metal-complex dye Thiotan TRN (Sandoz) is derived from chromium and is exclusively used in the colouration of carpets, retaining part of the chromium, while the rest substantially increases the waste-water load. The environmental impact of oxidised chromium caused by incineration, waste dumping or dye-house effluent is a matter of concern (Stakelbeck *et al.*, 2003). This has led to the development of Nylosan N-P dyes (Clariant) with lower chromium content. Iron(II) complexed Formazan dyes have been found to be eco-friendly, with all hue and shade ranges available. However, these dyes possess lower fastness compared to those obtained with chromium complexes. Aluminium complexed acid dyes have been synthesised but remain unapplied (Hooker *et al.*, 2003). Aluminium with cobalt and chromium shared complexed dyes show prominent deviation in both shade and fastness properties (Henning *et al.*, 1993).

In various chrome methods, dichromate is used in excess in order to guarantee maximum complex formation, which generates large amounts of solid content in the bath and subsequently in the waste water. The concentration of dichromates should be to the stoichiometric requirement. This is at least true with regard to the chrome method, where chroming being the last step permits reduction in effective concentration. Iron salts can also be used in these methods in place of dichromates, with good exhaustion and fastness. Even aluminium sulphate can produce shades with good wash fastness when used for complex formation (Julia *et al.*, 1993). Due to the attachment of the metal ion with the dye in premetallised dyes, efficient separation of unused dye will raise no concern of pollution.

### 13.9 Future trends

Metal-complexed acid dyes, especially 1:2 complexed with metal ions such as trivalent chromium, are extremely useful in dyeing protein and polyamide fibres to produce fast shades that are not possible with acid dyes complexed with other metal ions (the exception being acid dyes which are complexed with either cobalt or iron to some extent). Due to dyeing at a mild acidic pH, there is no risk of overdyeing and fibre damage. Poor coverage on wool, as well as the risk associated in dyeing with 1:1 complexed dyes because of the strong pH of the dyebath, has increased popularity of 1:2 complexed dyes.

The toxicity of metals, mainly cobalt and chromium, has raised concern about the generated waste-water load and its impact on the aquatic environment. Nylosan N-P dyes, based on the stoichiometric requirements of chromium, can reduce this load. Because of the promising contribution towards the exhaustion of baths, production of bright shades and excellent light and wash fastness, chromium will invariably remain the focus for producing these dyes. Iron-complexed dyes can replace chromium complexes, but only to a limited extent (Hannemann, 2001).

Reactive dyes are eco-friendly and are capable of producing superior wash-fast shades of unlimited hue on wool, through formation of covalent bonds with least damage to the fibre. However, the cost of dyeing is higher and the formation of level shades still remains a problem; production of the jet black shade has not seen success so far (Burkinshaw, 1992b).

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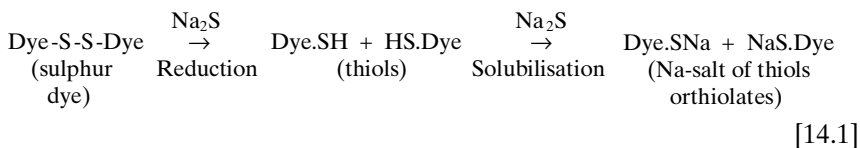
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Jalandhar, India

**Abstract:** Sulphur dyes are non-ionic, possess sulphur linkage, are water insoluble and produce shades that are reasonably cheap and wash and light fast. Dyes are applied in reduced and solubilised anionic state possessing affinity for cellulose. After dyeing, oxidation is carried out to restore parent non-ionic dye structure; sulphur dye-cellulose attachment is established through physical forces with dye aggregation occurring *in situ*. Shades lack tinctorial brilliance, limiting production to only deep shades like blue, black, khaki and green while brilliant red, orange and yellow are unsuccessful. Stored dyed cellulose is liable to be tendered in humid atmosphere due to presence of loose sulphur. Sodium sulphide, the most effective reducing/solubilising agent pollutes waste water, requiring the adoption of alternative reducing systems such as glucose, hydroxyacetone and reducing sugar.

**Key words:** sulphur dye, sulphur, reduction, sodium sulphide, tendering.

## 14.1 Introduction

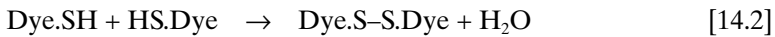
Sulphur dyes are chiefly used for dyeing cotton to medium or heavy shades, primarily because they achieve light fast and wash fast colours at low cost. Worldwide consumption of sulphur dye for use on cotton was found to be as high as 30% (Brooke, 1987). These dyes are non-ionic and insoluble in water. The desired anion is produced by reducing and solubilising at a high temperature, and it possesses an affinity for cellulose with a moderate strike rate. A single chemical like sodium sulphide ( $\text{Na}_2\text{S}$ ) suffices for the reduction and solubilisation alone: it severs sulphur linkages and breaks down dye molecules into thiols, then to sodium salts of thiol (also known as mercaptides or thiolates), which are soluble in water and substantive towards cellulose.



After dyeing, the textile is oxidised to restore the parent insoluble dye structure, which is retained by cellulose *in situ* as aggregates with H-bonds



and van der Waals forces of attraction.



Sulphur dyes are marketed under various brand names, and have been assigned C.I. constitution numbers ranging from 53 000 to 53 830 (SDC, 1987). Being a cheaper class of dye, regional manufacturers across the globe produce them to meet local demand.

## 14.2 Properties of sulphur dyes

Sulphur dyes are amorphous colloidal materials of high molecular weight and of variable composition. They are available in paste or powder form, insoluble in water, and cheap and easy to apply. Their substantivity towards cotton is somewhere in between that of vat and direct dyes.

Sulphur dyes show a wash fastness of around 4–5, and an overall light fastness of 5–6, with the exception of Black 1. Black 1 has a light fastness of 7, which can be further improved by after-treatment with metal salts like  $\text{CuSO}_4$ , and  $\text{K}_2\text{Cr}_2\text{O}_7$ , or a mixture of these two in an acidic pH. Shades produced by sulphur dyes are not fast to chlorinating agents, and are relatively dull and incomplete in shade range: true red, orange and violet are not available. Black, navy blue, khaki and olive green are the best shades. Light shades can be produced, but at the expense of brilliance and solidity. Dyed cotton is occasionally topped with basic dye or aniline black to brighten shades. The high alkalinity of the dyebath restricts the use of sulphur dyes on protein fibres, since these fibres degrade under such conditions.

Dyes exhaust best in the presence of electrolytes, at around 90–95°C.  $\text{H}_2\text{S}$  liberated during dyeing restricts the use of metal vessels, except stainless steel, because metals are liable to form corrosive metal sulphides that shorten the life of the container. The presence of loose sulphur causes sulphurous acid to develop if dye is stored in a humid atmosphere. A fall in pH will affect dye uptake, so a little  $\text{Na}_2\text{CO}_3$  is required in order to neutralise the dye before application.

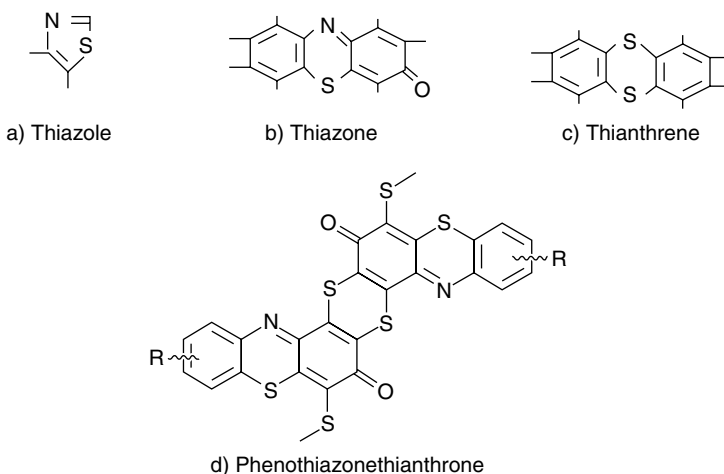
Sulphur dyes have important uses in dyeing garments and denim in rope form for high quality and performance. Expensive indigo can be partially replaced by blue sulphur dye through topping or bottoming, thus cutting costs without overly affecting fastness (Dixon, 1988; Stromberg, 1994). Failure to maintain proper conditions can lead to inefficient dyeing, which results in a bronzed appearance. Information on the development of sulphur dyes, and techniques to improve wash fastness, can be found in the

following sources: Burkinshaw and Collins, 1995; Burkinshaw *et al.*, 1996; Guest and Wood, 1989; Perkins and Crew, 1975; Wood, 1976.

Sulphur dyes can be identified by boiling a piece of dyed cotton along with  $\text{SnCl}_2$  (alternately Zn) and HCl in a test tube, while covering the mouth of the tube with a piece of filter paper soaked in lead acetate.  $\text{H}_2\text{S}$  forms, and reacts with the lead acetate to give PbS, which turns the paper black. Alternatively, dyed cotton may be treated with sodium or calcium hypochlorite when the colour is permanently discharged.  $\text{H}_2\text{SO}_3$  can develop on dyed cotton when it is stored, causing tiny holes in the cellulose due to local hydrolytic action.

### 14.3 Chemistry of sulphur dyes

The chemical structure of sulphur dyes is neither well defined nor consistent; it is determined by the raw material and the process used. Dyes retain sulphur linkages as the integral part of their chromophore and are basically a complex mixture of polymeric molecular species. These comprise a large proportion of sulphur in the form of sulphide ( $-\text{S}-$ ), disulphide ( $-\text{S}-\text{S}-$ ) and polysulphide ( $-\text{S}_n-$ ) links in heterocyclic rings. Chromophoric systems are mainly based on thiazole, thiazone and thianthrenes, while a few dyes retain phenothiazonethioanthrone as their chromophore, as illustrated in Fig. 14.1 (Allen, 1971; Christie, 2001). Excess loose sulphur develops sulphurous acid in a humid atmosphere and so needs to be isolated from the dye after synthesis.



14.1 Various chromophoric systems in sulphur dyes. (Fig. d has been reproduced by permission of the Royal Society of Chemistry.)

## 14.4 Synthesis

### 14.4.1 Sulphur dyes

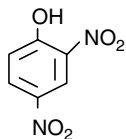
The manufacture of sulphur dyes involve sulphurisation, in which sulphur, polysulphide, or a mixture of both, is heated upto 180–350°C along with aromatic amines, phenols or aminophenols. Alternatively, the sulphur or sulphur compounds can be refluxed in solvents under pressure. Sulphurised vat dyes, an intermediate class between sulphur and vat dyes, are produced in the same way but their reduction requires a strong reducing agent like sodium hydro-sulphide (NaHS). Synthesis of sulphur dyes has been documented in many sources (Allen, 1971; SDC, 1987; Shankarling *et al.*, 1996). However, due to inconsistency in composition, they possess no definite chemical structure.

Sulphur Black BG/GXE/GXR (Bluish Black, C.I. Sulphur Black 1, C.I. 53185), the most important member, has the empirical formula  $C_{24}H_{16}N_6O_8S_7$  or  $C_{24}H_{16}N_6O_8S_8$ . It is produced by heating 2,4-dinitrophenol with sodium polysulphide (in proper ratio), at 110–120°C for 48–72 h under pressure (Fig. 14.2). The melt is diluted and black dye is precipitated either by the addition of acid or by air-oxidation.

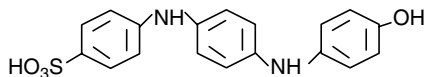
Sulphur Blue FBL (Blue, C.I. Sulphur Blue 10, C.I. 53470) is produced by heating N-[p-(p-hydroxyanilino) phenyl] sulphanilic acid with aqueous sodium polysulphide at 105–106°C for 100 h, and is precipitated by air blowing and the addition of salt at 70–80°C (Fig. 14.3).

Sulphur Green G/3G/GG (Green, C.I. Sulphur Green 3, C.I. 53570) is manufactured by refluxing 8-anilino-5-(p-hydroxyanilino)-1-naphthalene-sulphonic acid with aqueous sodium polysulphide at 106°C for 24 h, followed by precipitation through air blowing at 60–80°C (Fig. 14.4).

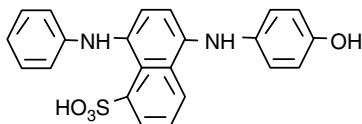
Sulphur Brown GS (Reddish Brown, C.I. Sulphur Brown 7, C.I. 53275) is obtained by reducing 1, 8-dinitronaphthalene with aqueous  $Na_2S$  at 90°C followed by baking at 270°C with sodium polysulphide,  $CuSO_4$  and NaCl (Fig. 14.5).



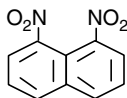
14.2 2, 4-dinitrophenol.



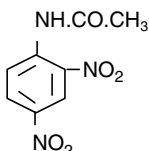
14.3 N-[ p-(p-hydroxyanilino) phenyl ] sulphanilic acid.



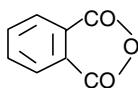
14.4 8-Anilino-5-(p-hydroxyanilino)-1-naphthalenesulphonic acid.



14.5 1,8-Dinitronaphthalene.



(a)



(b)

14.6 (a) 2',4'-Dinitroacetanilide; (b) phthalic anhydride.

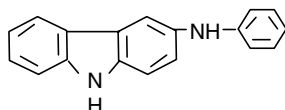
Sulphur Yellow G (Yellow, C.I. Sulphur Yellow 9, C.I. 53010) is produced by mixing 133 parts of 2',4'-dinitroacetanilide, 93 parts of phthalic anhydride, 280 parts of  $\text{Na}_2\text{S}$  and 94 parts of previously molten sulphur at  $95^\circ\text{C}$  (Fig. 14.6). Salt is then added and the mixture is heated up to  $130^\circ\text{C}$  for 10–11 h, beyond which it is heated up to  $180^\circ\text{C}$  and maintained for 3–4 h.

### 14.4.2 Sulphurised vat dyes

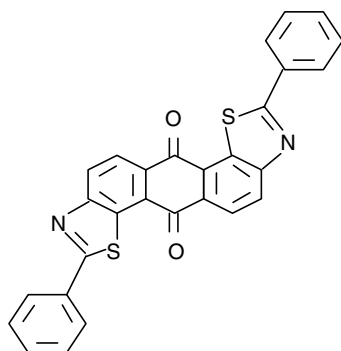
These are produced using the same sulphurisation process that is used for other sulphur dyes, but are reduced with  $\text{Na}_2\text{S}_2\text{O}_4$  and applied like vat dyes (Bernhardt, 1984; Heid, 1978). One commonly used example is Hydron Blue R (C.I. Vat Blue 43, C.I. 53630). Indophenol is produced by the condensation of p-nitrosophenol and carbazole in the presence of concentrated  $\text{H}_2\text{SO}_4$  at  $-20^\circ\text{C}$ : they are refluxed at  $107^\circ\text{C}$  for 24 h with sodium polysulphide in butanol to produce this dye (Fig. 14.7).

Hydron Blue R is an inexpensive substitute for indigo and cannot be completely reduced by  $\text{Na}_2\text{S}$ , so it is invariably reduced by  $\text{Na}_2\text{S}_2\text{O}_4$  in combination with  $\text{NaOH}$ .

Another example of sulphurised vat dye is Novatic Yellow 5G, C.I. Vat Yellow 2 (Atic). It is widely used to produce a greenish-yellow hue on



14.7 Indophenol.



14.8 Novatic Yellow 5G, C.I. Vat Yellow 2, C.I. 67300.

cotton, and is prepared by refluxing 2,6-diaminoanthraquinone, benzoin chloride and sulphur in naphthalene (SDC, 1987) (Fig. 14.8).

## 14.5 Classification of sulphur dyes

Sulphur dyes are classified according to chemical structure and application. The chemical classification includes pure sulphur dyes as well as sulphurised vat dyes. The first type only includes sulphur linkages and is reduced with  $\text{Na}_2\text{S}$ , while the second type includes both sulphur linkages and carbonyl groups, and is reduced with  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{NaOH}$ . Based on application, sulphur dyes are available in three main forms, namely, powder, reduced and water soluble. The powder form is the conventional insoluble type and is reduced and solubilised with  $\text{Na}_2\text{S}$  at the boil before application. Leuco sulphur dyes are physical mixtures of dye and  $\text{Na}_2\text{S}$ ; they require heating in water with a little excess  $\text{Na}_2\text{S}$  to reduce and solubilise the dye. The water-soluble or ready to apply liquid type is added directly to the bath, so that dyeing begins even at low alkali concentration. The last type is most suitable for continuous dyeing at low temperatures; they are free from fly-out (i.e. are not dispersed into the surrounding air, being liquid in nature), but are costly. These can be used in dyeing protein fibres too (Luo and Cao, 1997). This chapter includes details on manufacturing the first type; details of the last type have been discussed elsewhere (Teli *et al.*, 2001a).

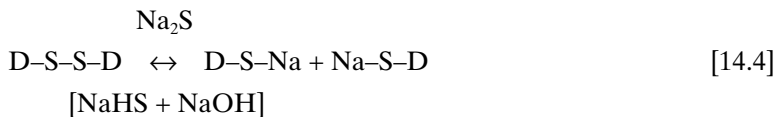
## 14.6 Practical application

### 14.6.1 Exhaust method

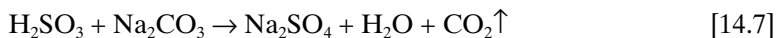
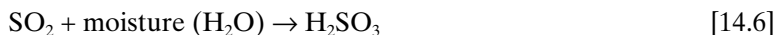
All sulphur and sulphurised vat dyes are exclusively applied using an exhaust dyeing method, because of the problems encountered are easily remedied: better diffusion and uneven dyeing can usually be repaired just by re-dyeing in the same bath or in a blank  $\text{Na}_2\text{S}$  bath at boil. The complete dyeing procedure includes a few stages, namely, reduction, dyeing, washing, oxidation, soaping and washing.

#### *Reduction*

The chemistry of reduction involves the conversion of sulphide, disulphide or polysulphide into leuco thiols. Dye is pasted with a little Turkey red oil to improve wetting and prevent the dye molecules from floating. Water is added, followed by a little  $\text{Na}_2\text{CO}_3$ .  $\text{Na}_2\text{S}$  is then added and the mixture is heated up to  $90\text{--}95^\circ\text{C}$  for 10–15 min to allow complete reduction and solubilisation of the dye, which is marked by the formation of stable foam on the surface of the liquor. The mechanism of reduction is believed to be through formation of  $\text{NaHS}$  and  $\text{NaOH}$  during hydrolysis of  $\text{Na}_2\text{S}$  in water;  $\text{NaHS}$  reduces dye and  $\text{NaOH}$  solubilises leuco dye to thiolates (Teli *et al.*, 2001b).



A stable reduced dyebath is highly alkaline, though the alkalinity may be partly lost due to the conversion of free sulphur in a humid atmosphere to  $\text{H}_2\text{SO}_3$ , which counteracts concentration of  $\text{NaOH}$ . The addition of a little  $\text{Na}_2\text{CO}_3$  neutralises this acid prior to reduction, avoids wastage of  $\text{Na}_2\text{S}$  and stabilises the dye in its reduced form.



The concentration of  $\text{Na}_2\text{S}$  required is based on its purity. Crude and flake grades have a purity of around 30–35% and 60%, respectively, and so almost double the amount of crude  $\text{Na}_2\text{S}$  is used for reduction and solubilisation. An increase in purity will necessitate a proportionally lower dose.

The use of iron vessels is restricted because the  $\text{H}_2\text{S}$  produced reacts with the metal to form iron sulphide, which in turn corrodes the dye vessel.



Over reduction of the dye with excess  $\text{Na}_2\text{S}$  causes the product to have less affinity for cellulose. A chelating agent, like ethylene diaminetetraacetic acid (EDTA), can be used to counteract interference from metals in hard water. The redox behaviour of Sulphur Black 1 was investigated using different reducing agents in order to understand and interpret dyeing results in practice (Bechtold *et al.*, 2000).

### *Dyeing*

Wet cotton is dyed in a reduced dyebath at  $90\text{--}95^\circ\text{C}$  for 30–60 min, after which salt (20–50 g/L) is added and dyeing is continued for further 1.5–2 h. The bath is drained out and the dyed cellulose is washed thoroughly in water. Due to the large amount of dye required to produce deep shades and its moderate affinity for cellulose, the dyeing time before and after salt addition should be kept on the higher side, to promote exhaustion of the bath.

Cotton dyeing is preferably carried out in a jigger or winch. Reduction takes place in the jigger itself. Four turns are given through the dyebath after which salt is added and a further eight turns are imparted at boil. The bath is dropped; dyed cotton is cold washed for two turns, then oxidised for two to four turns. This is followed by soaping, washing and padding with  $\text{CH}_3\text{COONa}$ . A detailed study of exhaust dyeing in jiggers and winches has been discussed in numerous research papers (Anon, 1987; Aspland, 1992a,b; Krauzpaul, 1987).

### *Oxidation*

Oxidation occurs in the presence of  $\text{K}_2\text{Cr}_2\text{O}_7$  (1–2 g/L) and  $\text{CH}_3\text{COOH}$  (1–2 mL/L) at  $50\text{--}60^\circ\text{C}$  for 30 min, when the dye returns to its parent oxidised form. The reaction between dichromate and acid produces the nascent oxygen required for oxidation.



Dichromate oxidation is cheaper, but stiffens dyed cotton through the deposition of chromium, and changes the tones of blue dyes. Sewing threads dyed with sulphur dye are often oxidised with  $\text{H}_2\text{O}_2$  to avoid stiffening; this in turn reduces needle cutting.

*After-treatment*

After oxidation and soaping, dyeings are passed through  $\text{CH}_3\text{COONa}$  at a lower liquor ratio, and are dried to counteract inorganic corrosive acid formed at the post-dyeing stage.



However, deposition of salt ( $\text{NaHSO}_3$ ) makes dyeings marginally stiffer. To improve light fastness, dyeings can be treated with metal salts in the presence of acid. Light fastness may also be improved by treatment with dye-fixing agents. Dull shades can be improved to some extent by topping with basic dye.

## 14.6.2 Continuous dyeing

Conventional sulphur dyes are not suitable for continuous application, due to the inconsistency in penetration of large amounts of dye to produce deep shades in a reasonably short time. Liquid sulphur dyes or micro-dispersed powdered sulphur dyes are most suitable for continuous dyeing of cotton. These are based on reduced and solubilised sulphurised vat dyes, which possess sulphur linkage as well as  $\text{C}=\text{O}$  groups, namely, Hydron Stabilisol dye (DyStar) and Diresul RDT liquids (Clariant). Hydron stabilisol dyes may be applied on mercerised cotton in a pad-steam process, with intermediate drying using caustic soda and sodium hydrosulphite. Polyester-cotton blends may be dyed in thermosol/pad-steam in single or two-stage processes. The blend is padded with a Samaron dyestuff (Hoechst) for polyester, followed by drying and thermosoling. It is then repadded with hydron stabilisol dyes with 40–60% liquor pick up, and steamed. Washing, oxidation and soaping are carried out as usual (Muller and Steinbach, 1986).

The Pad-Ox process developed by Clariant is a classic example of cleaner sulphur dyeing technology with three principal characteristics: minimum water consumption, reduced waste water and 100% dye pick up, leaving behind a colour-free waste water (Annen, 1998; Jimenez and Estape, 2003). In this method, dyeing is carried out with Diresul RDT dye, low sulphide based reductor D powder,  $\text{NaOH}$ , sandozine EH liquid and ladiquest 1097N liquid followed by fixation with diresul oxidant BR, acetic acid, indosol E-50, Ekaline and Glauber's salt. The viability of the method is based on the reaction of Indosol E-50 (fixing agent) with the thiol group and that of the oxidising agent with the quinone group; that is, by avoiding oxidation of the thiol group and any reaction between the fixing agent with the quinone.



Identical shade formation with parallel fastness properties has been claimed with little lowering of rubbing fastness. However, the cost of dyeing, and the difficulties associated with maintaining a stock of speciality chemicals, pose problems in continuous dyeing with sulphur dyes. Levafix CA dyes, marketed by DyStar, are low in salt and so reduce the solid content in discharged baths, thus maintaining dyeing efficiency parallel with other types of sulphur dyes.

Photografting with cationic monomers using UV radiation significantly enhances the dyeability of cotton with sulphur dyes. Cotton modified by this photografting technique showed increased dye pick up and better fastness properties when liquid sulphur dyes were used (Jang *et al.*, 2001). All the above-mentioned techniques result in a ring dyeing effect on cotton, thus reducing the quantity of dye as used in exhaust dyeing.

## 14.7 Reducing systems

Sulphur dyes require a reduction potential of around (–550 to –650) mV for proper reduction and the retention of a reduced form throughout the dyeing process (Bechtold *et al.*, 1991). Various reducing formulations are in place for this purpose; though a few of these are highly effective based on dye uptake and cost, but detrimental to the ecological balance.

### 14.7.1 Conventional reducing agents

$\text{Na}_2\text{S}$  alone and glucose (4 g/L) in combination with NaOH (2 g/L) are two effective formulations for reducing and solubilising sulphur dyes at 90–95°C. Reduced thiols are stable for a much longer time (Kaushik *et al.*, 1993). NaHS is another important reducing agent: the dosage is equal to that of  $\text{Na}_2\text{S}$  flakes but requires the addition of either of  $\text{Na}_2\text{CO}_3$  (10 g/L) or NaOH (5 g/L). In fact,  $\text{Na}_2\text{S}$  produces NaHS and NaOH when dissolved in water. Sodium hydrosulphite or dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ , 3 g/L) with NaOH (1.5 g/L) is a more powerful reducing agent than  $\text{Na}_2\text{S}$ , offering a reduction potential of around (–700) mV, and can cause over reduction resulting in the product having a poor affinity for cellulose. A few red-brown, green and olive dyes decompose in the presence of hydrosulphite, while some dyes give a better yield, but they have not been used for dyeing sulphur blacks because of reduced colour yield and poor reproducibility. Solubilised sulphur blacks can successfully be dyed using hydrosulphite but only at a higher cost. Leuco sulphur dyes and sulphurised vat dyes are often reduced with  $\text{Na}_2\text{S}_2\text{O}_4$ , resulting in an insufficiently stable bath, poor substantivity and dyeings possessing lower wash fastness.

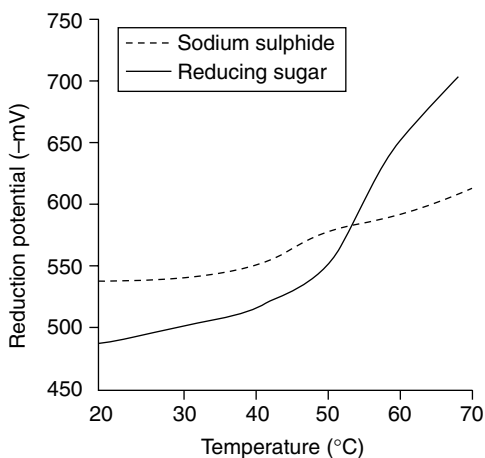
Other reducing agents, such as thioglycolic acid and thiosalicylic acid, though, are effective in certain cases but change the shades to some extent

(Klein, 1982). Sodium bisulphide keeps the dye bath in its reduced condition and prevents surface oxidation, reducing the chances of bronzing. Sodium sulphide, the cheaper and most efficient reducing agent, is associated with a huge waste-water load.

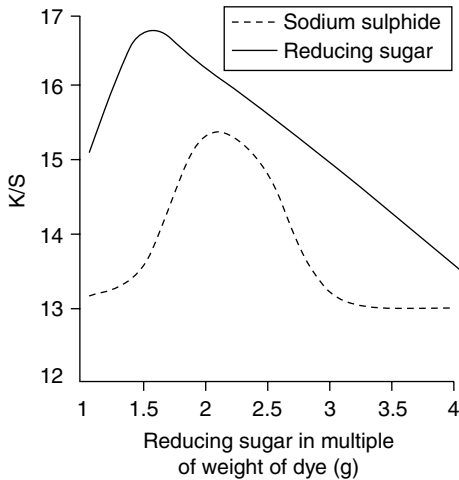
### 14.7.2 Sulphur-free reducing agents

In the electrochemical reduction of sulphur dyes, the cell current is regulated to control entry of the reducing agent to a bath. It is a cleaner technology and is superior for many reasons: (i) permits exact control over the dyeing process by potential measurement, (ii) controlled mass balance, (iii) no accumulation of reducing agent decay by-products, (iv) reproducible dyeing results, (v) reduced effluent problem, etc. (Bechtold and Burtscher, 1998).

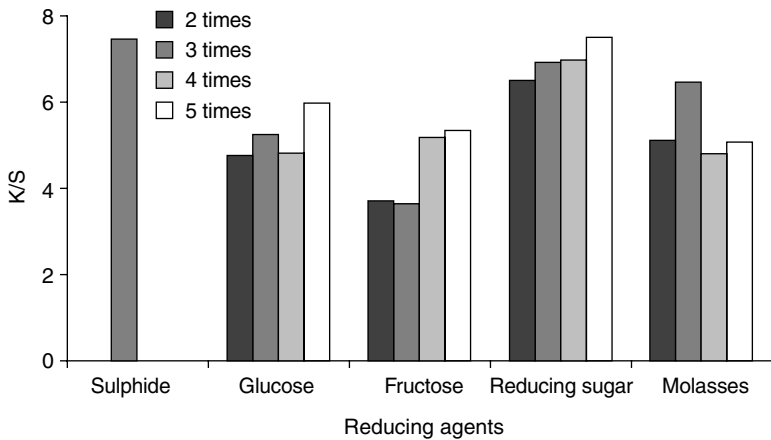
Glucose combined with NaOH results in poor dye uptake in jiggers and winches due to inconsistent temperatures above 90°C. Reducing sugar extracted from molasses produced a dye bath of constant stability with efficient dyeing in the presence of NaOH; the performance of the reducing sugar was observed to be superior to that of sodium sulphide, as shown in Figs. 14.9 and 14.10 (Chavan and Vhanbatte, 2002). The performance of non-sulphide reducing agents, i.e. glucose, fructose, reducing sugar (fructose), and that from molasses, were all found capable of complete reduction of the sulphur dye but with slightly reduced dye uptake. Sucrose was an exception: at five times the amount it resulted in a dye uptake equivalent to that with sulphide, as depicted in Fig. 14.11 (Shukla and Pai, 2004). In another attempt, an in-house



14.9 Effect of temperature on reduction potential of reducing sugar and sodium sulphide. (Reproduced by permission of *Indian Journal of Fibre and Textile Research*.)



14.10 Effect of concentration of reducing agent on Sulphur Black yield. (Reproduced by permission of *Indian Journal of Fibre and Textile Research*.)



14.11 Effect of various non-sulphide reducing agents on uptake of sulphur military green UI. Key: x times denotes weight of reducing agent to weight of dye x grams. (Reproduced by permission of *Indian Journal of Fibre and Textile Research*.)

preparation of reducing sugar by hydrolysis of edible cane sugar with HCl at pH 3.5 for 16 h at room temperature showed the best yield, in the form of a clear viscous solution with 80% conversion and clarity of product and was stable for three months. Dyeing results in terms of colour yield,  $L^* a^* b^*$  values and wash fastness properties, were found to be parallel to those obtained using sodium sulphide except with respect to tonal change. This could be

overcome by dyeing with reducing sugar alongside NaOH at 80°C, with intermittent addition of both during exhaustion (Chavan and Vhanbatte, 2004).

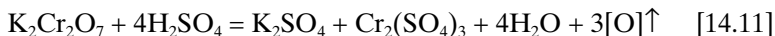
$\beta$ -mercaptoethanol in combination with NaOH results in efficient uptake when dyeing with leuco sulphur dyes in exhaust and pad-dry-steam processes. The process is free from odour but costly (Chavan, 2001).

Iron (II) salts react with NaOH to produce  $\text{Fe}(\text{OH})_2$ , generating a reduction potential of around  $-(700-750)$  mV. Though the potential range is adequate for the reduction of sulphur dyes, negligible solubilisation of iron cannot reduce dye to any remarkable extent.  $\text{Fe}(\text{OH})_2$  can be complexed with tartaric acid, citric acid, triethanolamine, etc. to hold  $\text{Fe}(\text{OH})_2$  in solution and to use it as a strong reducing agent at room temperature. However, the reduction potential becomes too high and causes over reduction (Chavan and Chakraborty, 2001; Semet *et al.*, 1995).

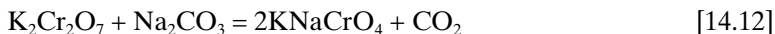
Hydroxyacetone generates a reduction potential as high as  $(-810)$  mV, is biocompatible and is applied in combination with NaOH. However, it is expensive and there is a chance of over reduction (Marte, 1989).

## 14.8 Oxidising agents

The two most commonly used oxidising agents are  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ . Three oxygen atoms are liberated when they are combined with an acid.



Overoxidation is possible as oxygen is formed rapidly. To slow down the process, a weak acid like  $\text{CH}_3\text{COOH}$  is used in place of  $\text{H}_2\text{SO}_4$  and the temperature is maintained at 50–60°C for 15–30 min. Before oxidation, a thorough wash is imparted to sulphur dyed goods to ensure the absence of alkali; the presence of a small quantity of alkali can hinder oxidation as  $\text{K}_2\text{Cr}_2\text{O}_7$  produces  $\text{CO}_2$  and not oxygen when it reacts with an alkali.



Both  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  are cheap, precipitate chromium on cellulose and impair the handle of dyeings. The stiffness developed results in more needle cutting and so sulphur dyed sewing thread is invariably oxidised with  $\text{H}_2\text{O}_2$ . In some cases, the tone of dyeings appears altered due to a reddish impression imposed – especially if blue shades are oxidised with dichromates. The application of metal salt, e.g.  $\text{CuSO}_4$ , improves light fastness a little but at the expense of handle and hence it is not preferred.

$\text{H}_2\text{O}_2$  is generally not used on cost grounds and for fear of over oxidation; only  $\text{H}_2\text{O}_2$  (1 mL/L, 35% or 130 V) at a pH of just above 7.0 and temperature of 50–60°C releases oxygen at a slower rate. Potassium iodate (1–5 g/L) at pH 4.0–5.0 adjusted with  $\text{CH}_3\text{COOH}$  at 60°C produces an excellent cold

pleasant black with soft handle and good fastness, but at higher cost. Both  $\text{H}_2\text{O}_2$  and  $\text{KIO}_3$  are eco-friendly oxidising agents. In fact  $\text{KIO}_3$  was at first suggested as the ideal oxidising agent for sulphur dyes (Klein, 1982).

### 14.9 Bronzing of dyeing

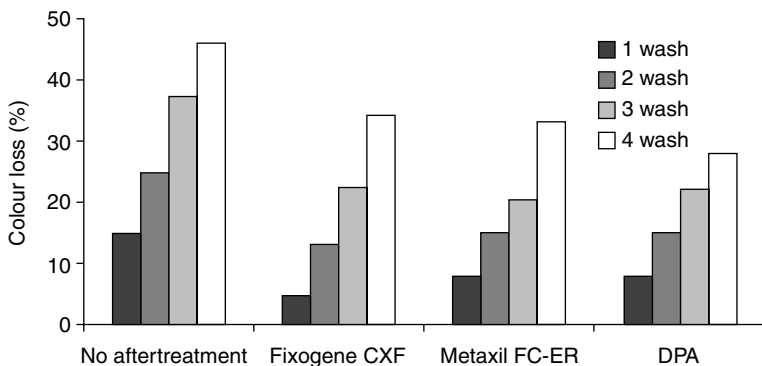
When viewed against a light, a bronze-like appearance is often visible on black and blue sulphur dyeings. This may be due to: (i) excessive heavy dyeing, when more and more dye molecules occupy surface areas only reflecting back more incident light, (ii) exposure of goods to air during dyeing, when layers of reduced dye form on the surface of cotton and are dried and oxidised, (iii) use of excess dye and (iv) inadequate  $\text{Na}_2\text{S}$  in the dyebath causing incomplete reduction. The root of this problem lies in insufficient diffusion of dye and more surface deposition. To rectify it, dye molecules must be distributed homogeneously, which can be achieved by re-dyeing cotton in a fresh bath with  $\text{Na}_2\text{S}$  at  $95^\circ\text{C}$  for 30–60 min at a lower liquor ratio, with 10% of the total dye used earlier.

### 14.10 Fastness of dyed textiles

The light fastness and wash fastness of sulphur dyed cotton are moderate to good. Deep shades accommodate a considerable amount of dye *in situ* fibre, part of which is discharged during washing with domestic bleach-containing detergent treatments, especially above  $50^\circ\text{C}$ . However, displaced colour molecules do not stain adjacent apparel in the washing machine due to their inherent non-ionic nature; dyeings fade during progressive laundering, but only lose depth of colour. Treatment with polymeric or conventional cationic dye-fixing agents can improve wash fastness in both batch and continuous methods, but the extent of improvement varies from one dye-fixing agent to another, as compared in Fig. 14.12 (Burkinshaw and Collins, 1998). After-treatment of dyeings in an unoxidised thiolate state with alkylating agents based on polyhalogenohydrins enhances washdown properties. In such cases, anionic dye molecules form complexes with the alkylating agent. So, unlike with conventional sulphur dyeing, no post-oxidation is required (Senior, 1995; Wood, 1976). However, changes in shade, decreases in light fastness and trouble in correcting faulty dyeings restrict the use of this technique. Topping of sulphur dyeings with vat dyes is mainly used to enhance brightness of shades, but improves wash and light fastness too.

Hypochlorite bleach destroys sulphur dye permanently, with the exceptions of sulphurised vat dyes and few reds, greens and blacks. However, in the latter cases, a remarkable amount of shade is discharged. Peroxide bleach also decolourises sulphur dyed shades but the action is not so severe (Senior, 1995).

Dry crock fastness is quite good (4–5), while wet crock fastness is inferior (2–3). Dyeing cotton in a jet dyeing machine improves wet crock fastness



14.12 Colour loss of dyeings with C.I. Leuco Sulphur Black 1 with and without after-treatment. (Reproduced by permission of the Society of Dyers and Colourists.)

considerably due to the hydrodynamic shearing action produced when fabric is passed through the jet nozzle and steel tubes of the jet (Tobin, 1979). Perspiration fastness grades are generally very good.

### 14.11 Tendering effect on cellulose

Sulphur dyed cotton retains some free sulphur and, if stored in a moist atmosphere, this oxidises to form  $\text{SO}_2$ .  $\text{SO}_2$  in turn absorbs moisture to form  $\text{H}_2\text{SO}_3$ , which creates tiny holes in the cellulose due to the local hydrolytic action of the acid.

This problem can be resolved by passing soaped and washed dyeings through a  $\text{CH}_3\text{COONa}$  bath at a lower liquor ratio so that  $\text{H}_2\text{SO}_3$ , as and when it is produced, will be converted to harmless  $\text{CH}_3\text{COOH}$ .



To assess the extent of tendering, the dyed sample is covered on both sides with two white pieces of cotton fabric, stitched, treated at  $140^\circ\text{C}$  for 1 min, and kept in air when the loose sulphur is oxidised with moisture from  $\text{H}_2\text{SO}_3$ . Stitches are removed, three pieces are separated out and each piece is tested for the presence of free sulphur and  $\text{H}_2\text{SO}_3$ .

### 14.12 Waste-water load from sulphur dyebath

A reduced and solubilised sulphur dyebath is not so complex in nature (Klein, 1982). An excess of sulphide, electrolyte and unused dye creates problems in the discharged liquor. Due to poor exhaustion of the dyebath,

the COD (chemical oxygen demand) of discharged liquor remains surprisingly high (Kaushik *et al.*, 1993).  $K_2Cr_2O_7$  in combination with  $CH_3COOH$  releases Cr(VI) compounds, which oxidise reduced dye molecules, and cause an increase in the solid content of the liquor. Waste-water load in terms of COD from a drained exhausted sulphur dyebath was found to be 534 mg  $O_2/L$  at a liquor ratio of 1:40, which was then reduced to 447 mg  $O_2/L$  when the liquor ratio was reduced to 1:20. The total COD, i.e. the combined COD values of all steps in the dyeing process, were 2002 and 2477, respectively; even higher than those for vat dyeing (Fiebig and Konig, 1977). Indeed,  $Na_2S$  and  $K_2Cr_2O_7$  are the chief causes of higher COD. Interestingly,  $Na_2S$  is the best reducing agent for sulphur dyes to date, and so effective methods were developed to remove unused sulphides from effluents.  $Na_2S$  can be easily oxidised to thiosulphate by atmospheric oxygen. The large quantity of sulphur dye present in the effluent catalyses the process, which has to be carried out in aerated tanks or reactors, where different effluents can be collected and equalised. A second method is precipitation in the form of iron sulphide. In practice, conversion is quantitative and the dyes present are also precipitated. Sulphur dyes can be precipitated by adding  $H_2SO_4$  to exhaust baths, which is then filtered off and reused. Analysis of dyeings where precipitated sulphur dyes were used shows the same composition, and gives consistent hues and levels of fastness (Spirkin *et al.*, 1981). For small industries, it would be cheaper to dye cotton with sulphur black using the glucose-NaOH system.

### 14.13 Strengths and limitations

The main advantage of using sulphur dye lies in their cheapness, even when producing deep shades on cotton with good wash and light fastness, compared against other classes of cotton dye. Consumption of costlier indigo in dyeing denim can be reduced by topping or bottoming with sulphur dye (Etters and Hurwitz, 1985). In topping, denim dyed with indigo to a lighter shade is re-dyed with sulphur dye to develop the desired shade. The bottoming process is just the opposite: denim dyed with sulphur dye is then re-dyed with indigo, with the sulphur dye remaining at the bottom of the indigo layer. The top or bottom can be accomplished by applying sulphur dye in the pre-wash, final indigo bath, or in the after-treatment section (Stromberg, 1994).

There are many limitations associated with sulphur dyes: (i) inadequate tinctorial ability limits production of light shades, (ii) limited hue range – true red, orange and yellow cannot be produced, (iii) shades lack brightness (though this can be manageably improved by topping with basic dyes), (iv) bronzing due to heavy dyeing, (v) tendering of cotton on storage in a humid atmosphere, (vi) not applicable on swimming costumes for fear of

decolourisation and (vii) not applicable on protein fibres due to the high alkalinity of the bath.

#### **14.14 Stripping of sulphur dyes**

Treatment with sodium hypochlorite or bleaching powder solution (1.5–3 g/L available chlorine) causes decolouration of sulphur dyeings to varying extents. The majority of dyeings are completely decolourised. The remaining few, as well as all sulphurised vat dyeings, are remarkably faded resulting in dull shades. Fading is less severe when treated with hydrogen peroxide (Senior, 1995). The loss in colour value has been proposed as over oxidation, and may be due to action of hypochlorous acid formed through dissociation of hypochlorites with the fall in pH in the open air. Potassium permanganate also causes decolouration of sulphur dyeings in the same way as hypochlorites. However, partial stripping of dyes and correction of faulty dyeings may be achieved with sodium sulphide, or with a combination of sodium hydrosulphite and sodium hydroxide at boil, for powder and soluble sulphur dye, respectively (Shenai, 1987).

#### **14.15 Future trends**

Being a highly cost-effective process with promising fastness ratings (except chlorine), sulphur dyeing will remain one of the main dyeing choices in spite of its negative ecological impact. This is due to the absence of any equivalent alternative technology. The cheaper cost of dyes and chemicals, fastness of dyeings, as well as the effectiveness of dyes in topping and bottoming on denim to ease bio-washing, will play a vital role in the continued use of these dyes. Ecologically friendly technologies are being developed by synthesising modern sulphur dyes through thionation in an aqueous medium. New application techniques, such as the 'Acqualess process' for continuous dyeing, 'exhaust dyeing under nitrogen atmosphere', etc., have also been developed using non-toxic auxiliaries (Annen, 1998; Kubanik, 1998). A low ecological impact is being claimed because the dyes are free from heavy metals and AOX, have no dyeing odour and a short liquor ratio. There is also little or no colour in the effluent due to high exhaustion rate, and low fish toxicity.

Adequate research is still needed on how to escape the problem of chromium deposition. One solution lies in replacing sulphide with reducing sugar or other sulphur-free reducing systems and dichromates with iodates at lower concentrations. Electrochemical reduction is another alternative technique to replace sulphide for reduction. Vat dyes could replace sulphur dyes, especially for black, but are too expensive in practice. Perhaps in the future all cotton blacks will be dyed with sulphur black, either by topping with vat black or with aniline black, which is used as a fraction at present to improve the fastness and brightness of dyeings.



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**Abstract:** Definition and classification of acid dyes are discussed. Chemistry of azo, anthraquinone, nitrodiphenylamine, triphenylmethane and xanthenes dyes are discussed.

**Key words:** anionic dyes, acid dyes, washfastness, lightfastness, water repellent, of azo, anthraquinone, nitrodiphenylamine, triphenylmethane and xanthenes dyes

## 15.1 Introduction

The name 'acid dye' originates from the dyeing process, which is carried out in acidic (pH 2.0–6.0) aqueous solution. Acid dyes or anionic dyes include many compounds from the most varied chromophoric systems which exhibit characteristic differences in structure but possess as a common feature water-solubilising ionic substituents.

Almost invariably the products that are manufactured and used are water-soluble sodium salts of sulphonic acids, the main reason being that they are readily introduced and, as strong electrolytes, are completely dissociated in the acidity range used in the dyeing process. Recently sodium salts of carboxylic acids have become important as dyes for ink-jet printing. These dyes are therefore anionic in solution. Most premetallised and mordant dyes are also acid dyes.

The anionic dyes in principle include direct dyes, but, because of their characteristic structures these are used to dye cellulose containing materials and are applied to the fibre from a neutral dyebath. The group of anionic dyes also includes a large proportion of reactive dyes, which in addition to the usual structural characteristics also contain groups that can react with functional groups of the fibre during the dyeing process.

Acid dyes will dye fibres with cationic sites such as wool, silk and nylon. Protein fibres contain amino and carboxyl groups, which in the isoelectric range (pH 5.0), are ionised mostly to  $\text{NH}_3^+$  and  $\text{COO}^-$ . In the acid dyebath the carboxylate ions are converted to undissociated carboxyl groups owing to the addition of acid giving the positively charged fibre  $\text{H}_3\text{N}^+ - \text{F} - \text{COOH}$  to take an equivalent amount of acid anions. Dyeing involves exchange of the anion associated with ammonium ion in the fibre with a dye anion. The dye anions exhibit a greater affinity for the substrate than the much smaller

acid anions. The dye is thus bonded to the wool not only by electrostatic attraction (salt formation) but also by its affinity for the fibre. Dyeing is therefore not solely a consequence of simple ionic interaction.

## 15.2 Classification of acid dyes

### 15.2.1 Classification according to affinity

The absorption of dyes by polyamide fibres involves the ionic interaction of the dye with the hydrophobic groups in the fibre together with the electrostatic attraction. Therefore their differences in affinity are primarily a function of molecular size. Based on the affinity three different classes are recognised:

1. Levelling dyes form a salt-like bond with the protein fibre and are relatively small molecules.
2. Milling dyes for which salt formation with the fibre and the adsorption forces between the hydrophobic regions of the dye molecules and those of the protein fibre predominate. They are the large volume molecules.
3. Dyes which not only form a salt-like bond with the wool fibre but also bonded to the fibre by intermolecular forces. They have properties lying in an intermediate position between those of the levelling and milling dyes with intermediate molecular size.

### 15.2.2 Classification according to dyeing characteristics

Dyeing characteristics of acid dyes allow them to be categorised into the following four types:

1. Level dyeing or equalising dyes
2. Fast acid dyes
3. Milling acid dyes
4. Super-milling acid dyes.

The molecular weight and degree of sulphonation of the dye molecule determine the dyeing behaviour such as the pH of dyeing, migration ability to dyeing and their washing fastness.

#### *Levelling or equalising acid dyes*

These dyes require considerable amounts of strong acids along with Glauber's salt to achieve good exhaustion. Under the high concentration of acid high concentration of cationic ammonium groups are generated in the

wool and the dyes have rapid strike for the wool. The dye molecules, however, are not strongly bound to the sites. Initial non-uniformity in colour is evened out by their good migration at the boil.

As a consequence of ease of migration these dyes have poor to moderate wash fastness. The light fastness, however, ranges from fair to good. This group of dyes is thus used for pale to medium depths on wool fabrics and yarn where a high degree of levelness only is critical and not good fastness to washing. They are brighter compared to mordant or metal-complex dyes. They have relatively small molecular size and hence have good water solubility. They have good penetration into individual fibres of tightly woven fabrics and high twist yarns. The dye molecules do aggregate in solution and at higher temperatures enough individual molecules are present for good penetration.

#### *Fast acid dyes*

Compared to the typical levelling dyes fast acid dyes are of somewhat higher molecular weight and are usually monosulphonated ones. The dyeing method is also similar. They have reasonable migration at boil, and sometimes a levelling agent is recommended. Fast acid dyes are used when level dyeing is necessary with good washing and perspiration fastness.

#### *Milling acid dyes*

Milling is the process in which a woollen material is treated in weakly alkaline solution, with considerable mechanical action to promote felting. Dyes of good fastness to milling are necessary to avoid bleeding of colour during the milling.

Milling dyes have higher molecular weights and greater substantivity for wool than levelling or fast acid dyes. They have fewer sulphonate groups per dye molecule and hence they have lower water solubility. They have a strong tendency to aggregate even in boiling water giving colloidal solutions. Dyeing with milling dyes is usually started in the presence of sodium acetate or ammonium sulphate and is carried out in the pH range from 5.0 to 7.0. The exhaustion is increased by the addition of acetic acid. They have low rates of diffusion in wool and hence poor levelling ability. Other than the ionic bonding there exist intermolecular forces between the dye and the fibre. Milling acid dyes give moderate to good washing fastness and as expected are better than the levelling acid dyes. Specifically they are fast to alkaline milling and have fairly good light fastness.

Since they have poor migration properties, level dyeing initially depends upon gradually increasing the dyebath temperature, and then lowering the pH of the dyebath by the addition of a small amount of acetic acid. These dyes tend to stain cotton. They are often preferred for self-shades as they have poor dyeing compatibility in mixtures.

*Super-milling acid dyes*

These are similar to milling dyes but much more hydrophobic. The hydrophobicity is manifested due to the presence of long-chain alkyl groups in the molecule. They have good wash fastness, and good to very good light fastness. They are used for yarn dyeing when there is a requirement of scouring and milling of the final fabric.

Milling and super-milling dyes have very rapid absorption behaviour resulting in unlevel dyeing, and they do not migrate easily. The rate of absorption of the dye needs to be controlled by gradual increase in the dye bath, followed by gradual decrease in the pH of the dye bath. The initial pH of the dye bath must be even higher than 7.0 for dyeing pale shades to mitigate the initial strike. The pH can be lower in case of dyeing loose fibre and tops where levelness is less critical since the fibre will be blended together during spinning. Dyeing rate with these dyes increase rapidly above 70°C, once the dye aggregates in solution begin to break up with increasing temperature. A careful control of temperature at this critical stage gives even dyeing.

### 15.2.3 Classification according to chemical constitution

Acid dyes are drawn from many different chromophoric systems. They are as follows:

- Sulphonated azo dyes
- Anthraquinone dyes
- Nitrodiphenylamine dyes
- Triphenylmethane and xanthenes dyes.

Sulphonated copper phthalocyanine dyes provide bright turquoise shades.

## 15.3 Azo acid dyes

Sulphonated azo dyes constitute the major group and are mainly mono- and bisazo dyes ranging in colour from yellow, through red to violet and brown. There are some navy blue bisazo dyes that can build up to give blacks. The substantivity of anionic azo dyes for polyamides and protein fibres is greater the higher their molecular weight and the lower the number of sulphonic acid groups in the dye molecule. There are several acid mordant and metal-complex dyes.

There are a number of acid and direct dyes with similar structural features in the azo class. These dyes will dye wool, nylon and cotton. An important feature that distinguishes acid dyes from direct dyes, apart from their lower molecular weights, is that molecular planarity is not essential for acid dyes while it is a requirement for direct dyes.

### 15.3.1 Monoazo acid dyes

There are a number of monoazo acid dyes distinguished by brilliance of shade, very good levelling power and particularly low cost. They possess no outstanding colouristic properties and their light and wash fastness meet only low to medium requirements. However, in recent years, partly influenced by the introduction of the International Wool Label to label high-quality wool articles, the fastness requirements have gone up considerably, and several fast dyes have been developed.

In the manufacture of monoazo acid dyes usually aniline derivatives are used as the diazo components. The coupling components for orange to blue shades are usually aniline, naphthol, naphthylamine and aminonaphthol derivatives, while N-phenylpyrazol-5 ones are used for preparing yellow and orange dyes.

Azo dyes with free OH and NH<sub>2</sub> groups are sensitive to alkali and acid, respectively. In commercial dyes these groups occur ortho to the azo group in order to form a hydrogen bond with the latter. This hydrogen bond prevents a dissociation of the hydroxyl groups or a protonation of the amino groups and hence they are not pH-sensitive.

One of the oldest azo dyes is C.I. Acid Yellow 36, C.I. 13065 [487-98-4] (1). For economic reasons 1 is used for dyeing wool and in special applications (leather and paper) in spite of lower fastness to acid.

Coupling of diazotised H-acid to 1-(phenylamino) naphthalene-8-sulphonic acid (N-phenyl peri acid) yields C.I. Acid Blue 92, C.I. 13390 [3861-73-2] (6). It gives a pure blue colour on wool with good light fastness, moderate wash fastness and adequate levelling power.

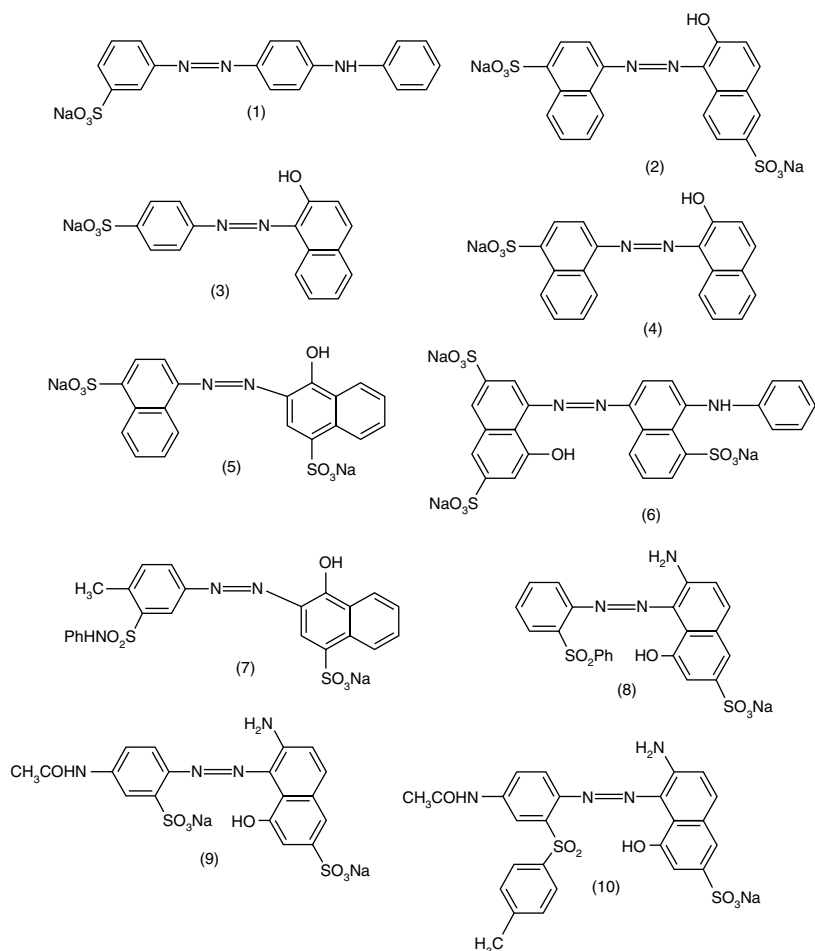
A series of two important dyes with very similar structure comprises C.I. Acid Red 88, C.I. 15620 [1658-56-6] (4), obtained from diazotised naphthionic acid and 2-naphthol, and C.I. Acid Red 13, C.I. 16045 [2302-96-7] (2), from diazotised naphthionic acid and Schaeffer's acid. They give attractive red shades and are used in textile dyeing and also as leather and paper dyes. They exhibit only moderate fastness properties.

C.I. Acid Orange 7, C.I. 15510 (3), popularly known as Orange II, is one of the oldest dyes. It is used more in special areas like leather and paper dyeing. The dye C.I. Acid Red 14, C.I. 14720 [3567-69-9] (5) is used for inexpensive articles in wool dyeing to a limited extent.

Introduction of large volume substituents on these simple dyes improves the wet fastness of the dyes at the expense of levelling ability. An example is C.I. Acid Orange 19, C.I. 14690 [3058-98-8] (7), which has good fastness properties together with good levelling power on wool and polyamide.

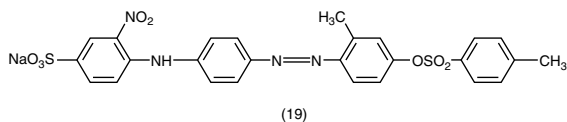
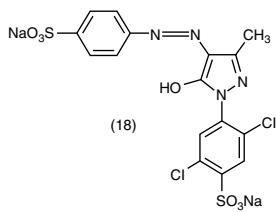
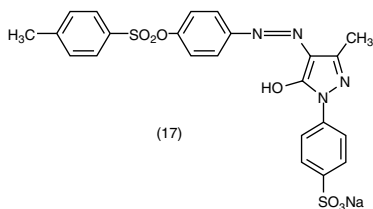
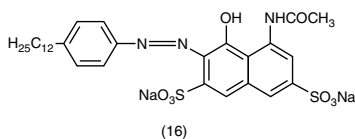
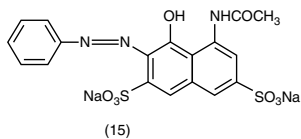
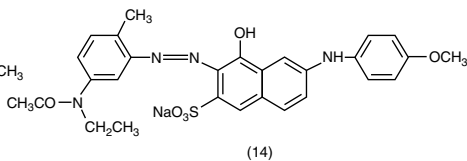
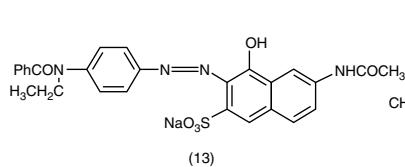
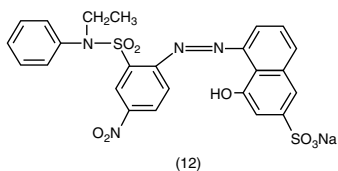
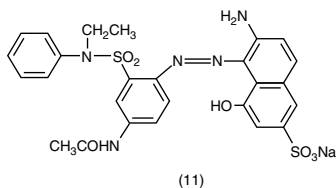
Monoazo acid dyes derived from aminonaphthol sulphonic acids like gamma acid and H-acid as coupling components exhibit very good light and wet fastness. Especially, acid coupling of gamma acid yields dyes with very





### 15.1 Monoazo acid dyes.

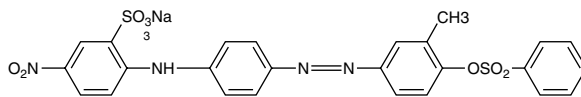
good light fastness, which is presumably attributable to the formation of a hydrogen bond between the azo bridge and hydroxyl group adjacent to the azo bridge. Two such dyes of outstanding light fastness and good levelling power with moderate wash fastness are C.I. Acid Red 42, C.I. 17070 [6245-60-9] (8) and C.I. Acid Red 37, C.I. 17045 [6360-07-2] (9). In this series by the choice of suitable substituted diazo components, bluish red to blue wool dyes with good light and wet fastness can be produced, for example, C.I. Acid Violet 14, C.I. 17080 [4404-39-1] (10). Further examples in this series are C.I. Acid Red 32, C.I. 17065 [6360-10-7] (11) and C.I. Acid Blue 117, C.I. 17055 [10069-12-7] (9). There is continued interest in acid dyes of this type (Blus, 1999).



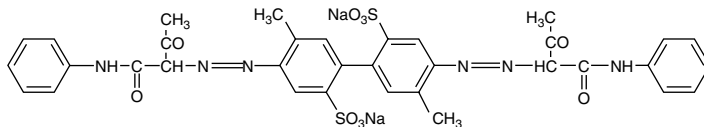
### 15.2 Monoazo acid dyes with enhanced wash fastness.

Alkaline coupling of gamma acid where amino group is either acylated or arylated gives valuable dyes. An example is C.I. Acid Red 68, C.I. 17920 [6369-40-0] (13). N-arylation of gamma acid gives a strong deepening of the shade. It gives mainly brown to black dyes with good light fastness and milling fastness. An example is C.I. Acid Brown 20, CI 17640 [6369-33-1] (14).

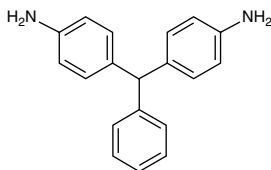
H-acid is an important coupling component in the synthesis of acid dyes. Acylation of amino group in H-acid substantially improves the light fastness of the dyes obtained therefrom. These dyes have good levelling power, and light fastness as well as wet fastness. Valuable dyes are also obtained with N-benzoyl-H-acid and N-toluenesulphonyl-H-acid. A relatively simple structure is exemplified by C.I. Acid Red 1, C.I. 18050 [3734-67-6] (15). Incorporation of long hydrophobic hydrocarbon residues yields dyes with



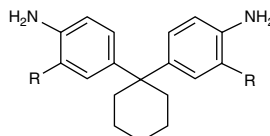
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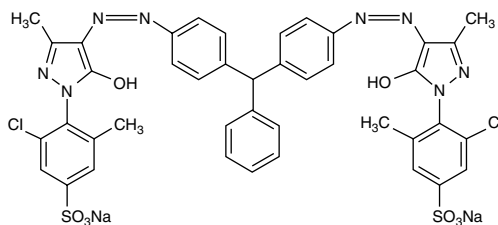
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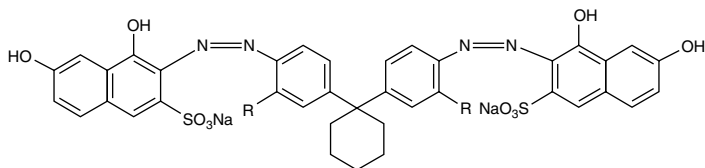
(22)



(23) R = H

(24) R = CH<sub>3</sub>(25) R = OCH<sub>3</sub>

(26)

(27) R = CH<sub>3</sub>(28) R = OCH<sub>3</sub>

### 15.3 Bisazo acid dyes and their intermediates.

neutral affinity and good wet fastness properties as in C.I. Acid Red 138, C.I. 18073 [15792-43-5] (16). Acid dyes with dodecyl or dodecyloxy groups (Carbolan dyes) were developed by ICI and are characterised by high milline fastness, a property conferred on the molecule by the long-chain alkyl groups (Abrahart, 1977, p. 97; Venkataraman, 1970, p. 268). It has been found that long-chain alkyl groups increase the water repellency and

decrease the substantivity of dyes on cotton and wool fibres through steric hindrance (Chao and Yeh, 1993; DeWitt and Shroff, 1953). Acid dyes with arylsulphonamide groups have been continuously studied (Blus and Kraska, 1988, 1992, 1993; Kraska and Blus, 1984). Dyes with an arylsulphonanilide group dye polyamide and protein fibres from weakly acidic dyeing baths give a very high degree of dyebath exhaustion. The colour and constitution relationships in C.I. Acid Red 138 and its homologues have been studied (Stoyanov *et al.*, 1995).

Light-fast yellow dyes are obtained using 1-phenylpyrazol-5-one coupling components (Schwander, 1982). The first representative in this series is Tartrazine, C.I. Acid Yellow 23, C.I. 19140 [1934-21-0]. Tartrazine is prepared from 1-(phenyl-4-sulphonic acid)-3-carboxy-5-pyrazolone as the starting material which is prepared from oxaloacetic ester and phenylhydrazine-4-sulphonic acid and coupling with diazotised sulphanilic acid.

Dyes based on 1-aryl-3-methylpyrazol-5-ones and their derivatives are cheaper compared to the corresponding 3-carboxypyrazolones. An example is C.I. Acid Yellow 17, C.I. 18965 [6359-98-4] (18), which gives a clear, light-fast yellow with good to very good general fastness properties.

C.I. Acid Yellow 76, C.I. 18850 [6359-88-2] (17) is a milling dye. It is obtained by coupling diazotised 4-aminophenol into the pyrazolone component and then esterifying with *p*-toluene sulphonic acid chloride in an alkaline medium. Better milling fastness is due to the presence of toluene sulphonic ester group. Yellow acid dyes derived from 1-phenyl-3-methyl-5-pyrazolone and containing two arylsulphonamide groups have also been synthesised (Blus, 1992).

Monoazo dyes from heterocyclic diazo components as well as coupling components are not so common in acid dyes of commercial importance except those derived from pyrazolones. However, there is academic interest in this area. 5-Substituted-2-thiobarbituric acid has been mentioned as a coupler and a series of acid dyes is known (Akiyama *et al.*, 1987). Monoazo acid dyes from 4-aminonaphthalimide (Wojciechowski, 1993) and 5.10-dihydroxyphenophosphazine (Zhi-Gang *et al.*, 2009) are reported. 2-Aminobenzothiazoles containing a sulphonic group has been mentioned as a useful diazo component for acid dyes in the patent literature (Gerhard and Guemter, 1977; Gerhard and Richard, 1975; July and Zelek, 1967; Niegel, 1980a,b; Weaver, 1974). It has been claimed that these dyes are compatible with the anthraquinone based dyes (Gerhard and Richard 1975). *N*-Phenylindole based couplers have also been used in obtaining yellow and orange dyes (Niegel, 1980a,b; Weaver, 1974). 3-Amino-7-nitro-2H-1,2-benzothiazine-1,1-dioxide has been used in obtaining acid dyes as well as chromable dyes having high tinctorial strength (Rajagopal and Seshadri, 1990).

### 15.3.2 Disazo acid dyes

Primary disazo dyes are obtained according to the scheme  $A_1 \rightarrow Z \leftarrow A_2$  from a bifunctional coupling component  $Z$  and two identical or different diazo components  $A_1$  and  $A_2$  or according to the scheme  $C_1 \leftarrow D \rightarrow C_2$  by coupling a bis diazotised diamine  $D$  to the coupling components  $C_1$  and  $C_2$ , which may be the same or different. Secondary disazo dyes are obtained according to the scheme  $A_1 \rightarrow M \rightarrow C$  (where  $M$  is the middle component) from diazotised amino azo dyes ( $A \rightarrow M$ ) and a coupling component  $C$ .

#### *Primary disazo dyes of the type $A_1 \rightarrow Z \leftarrow A_2$*

H-acid is an important dual coupling component used in the disazo acid dyes. The shade variation is very little in this series; mainly black, dull brown and blue dyes are obtained. They are the completely conjugated chromophores.

C.I. Acid Black 1, C.I. 20470 [1064-48-8] (32) is one of the important acid dyes. It dyes wool in blue-black shades with very good light fastness and exhibits high affinity and good levelling power but only moderate wet fastness. It has remained an important dye that forms the basis of black acid dyes.

#### *Primary disazo acid dyes of the type $C_1 \leftarrow D \rightarrow C_2$*

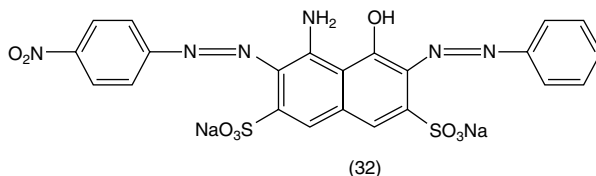
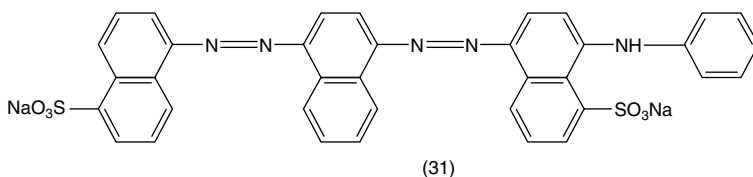
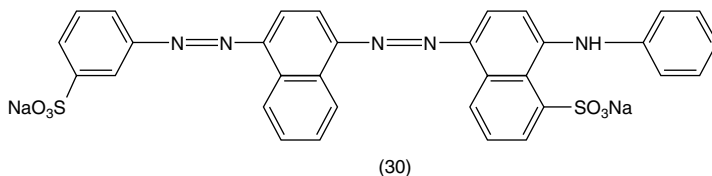
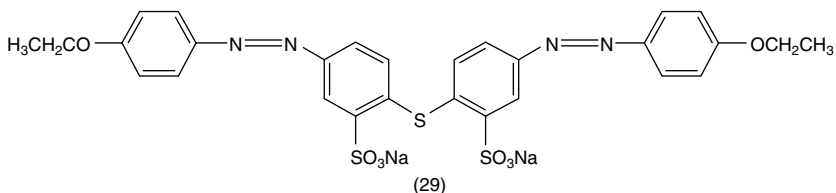
These dyes include many milling dyes. This is due to the fact that molecular size can be varied by suitable variations. When phenols, pyrazolones, acetoacetic acid arylamides or naphthol sulphonic acids are used as coupling components clear yellow to red shades are obtained.

Diamino diphenyls substituted at 2,2' positions give wash-fast and milling-fast acid dyes. An example is C.I. Acid Yellow 44, C.I. 23900 [2426-76-7] (21). C.I. Acid Yellow 42, C.I. 22910 [6375-55-9] is also an important example of this type.

Special diamines developed for the synthesis of disazo acid dyes of this type are 22, 23, 24, and 25. Dyes based on these compounds have good light fastness, and excellent wet fastness. They are usually neutral dyeing but play an important role in dyeing blended spun yarn and blended fabrics of wool and cotton or wool and viscose staple. The neutral dyeing acid dyes can be used in combination with direct dyes. Examples are C.I. Acid Yellow 56, C.I. 24825 [6548-24-9] (26), C.I. Acid Red 154, C.I. 24800 [6507-79-5] (27) and C.I. Acid Red 134, C.I. 24810 [6459-69-4] (28). A milling dye is exemplified by C.I. Acid Yellow 38, C.I. 25135 [13390-47-1] (29). Disazo acid dyes derived from 3,3'-diaminodiphenylsulphone have been reported (Rajagopalan *et al.*, 1988).

#### *Secondary disazo dyes of the type $A_1 \rightarrow M \rightarrow C$*

There exist much greater possibilities for variations than the primary disazo dyes. Red dyes and, above all, navy blues and blacks are found in this series.



#### 15.4 Disazo acid dyes.

Black, and navy blue wool dyes in this series contain 1-naphthylamine or 1-naphthylamine-7-sulphonic acid as middle components and N-phenyl peri acid and N-tolyl peri acid, and naphthol and 1-naphthylamine derivatives as coupling components. They are the very wash-fast and light-fast dyes. Examples are C.I. Acid Black 24, C.I. 26370 [3071-73-6] (30), C.I. Acid Blue 113, C.I. 26360 [3351-05-1] (31) and C.I. Acid Black 26, C.I. 27070 [6262-07-3].

#### 15.3.3 Chrome dyes

The chroming of largely acid monoazo dyes with certain structural features converts them into chromium complexes on the fibre which improves the light fastness as well as wash fastness of the dyeing. It also results in a deepening and dulling of the shade.

The application of chrome dyes to the fibre involves after-chroming, wherein the dye is allowed to go onto the fibre from an acid bath followed by treatment with dissolved alkali metal dichromate. In some special cases a

one-bath chroming method (metachrome process) is followed. Chrome dyes are only of very limited commercial importance today for ecological reasons.

Salicylic acid based dyes are mainly yellow and orange. Examples are C.I. Mordant Yellow 1, C.I. 14025 [584-42-9] (33) and C.I. Mordant Yellow 5, C.I. 14130 [6054-98-4] (34). The complex formation on the salicylic acid group has little influence on hue and light fastness, as against the *o,o'*-disubstituted arylazo compounds.

Metal complexation of *o,o'*-disubstituted arylazo compounds brings about a considerable deepening of shade and usually increases the light fastness. Examples are C.I. Mordant Red 7, C.I. 18760 [3618-63-1] (35) and C.I. Mordant Red 19, C.I. 18735 [1934-24-3] (36). Two other important black dyes are C.I. Mordant Black 3, C.I. 14640 [3564-14-5] (38) and C.I. Mordant Black 11, C.I. 14645 [1787-61-7] (40). Other examples are C.I. Mordant Blue 13, C.I. 16680 [1058-92-0] (37) and C.I. Mordant Black 9, C.I. 16500 [2052-25-7].

The *o,o'*-dihydroxy aminoazo and *o*-hydroxy-*o'*-aminoazo compounds with phenols or aniline derivatives as coupling components give mainly brown shades on after-chroming. C.I. Mordant Brown 33, C.I. 13250 [3618-62-0] (41) is an example.

Some dyes that are suitable for the one-bath chroming method (metachrome process) are C.I. Mordant Yellow 30, C.I. 19360 [6359-71-3] (43), C.I. Mordant Brown 48, C.I. 11300 [6232-53-7] (44) and C.I. Mordant Blue 7, C.I. 17940 [3819-12-3] (45). Compared with the after-chrome method metachrome dyeing has the advantage of simple application process. The hydrophilic character and its rate of complex formation decide the suitability of the dye to the metachrome process.

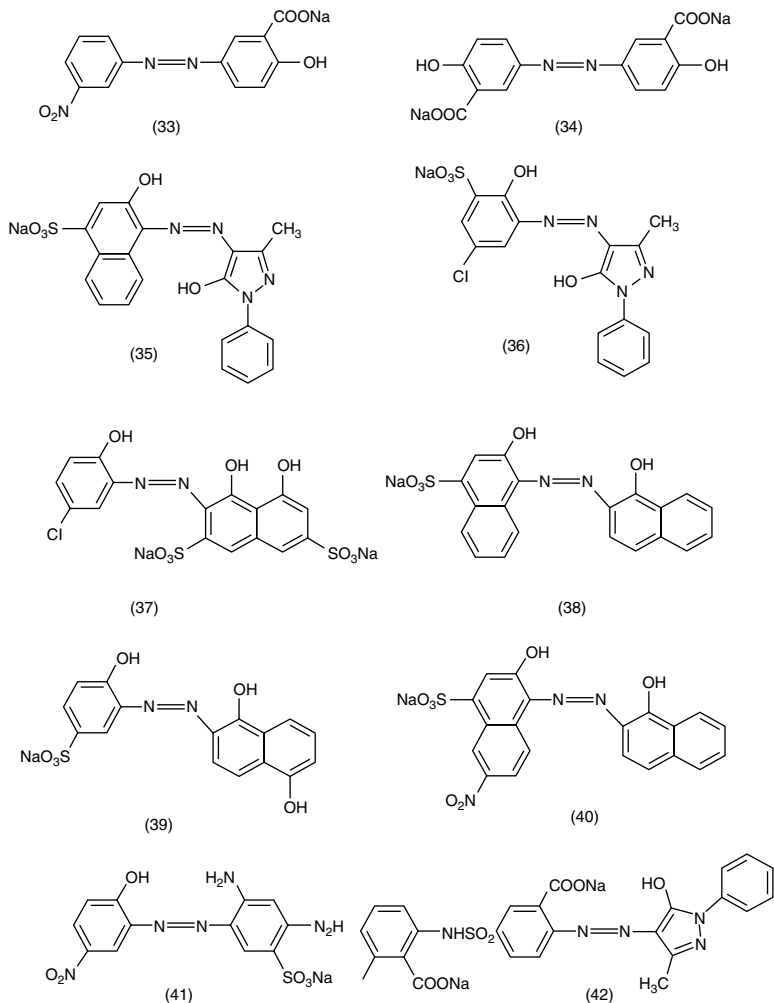
### 15.3.4 Acid dyes for synthetic polyamides

Polyamide materials of synthetic origin can be dyed with disperse dyes, and with selected acid dyes including metal-complex dyes. Synthetic polyamides have lower acid-binding power and hence dyes with two or more sulphonic acid groups in the molecule go onto the fibre much more slowly and to a much lower saturation value than dyes with one sulphonic acid group.

As with acid dyes for wool, the acid dyes for synthetic polyamides fall into two classes:

- Group A consists of acid dyes with good levelling power and low substantivity for polyamide; they give reasonably good wet fastness.
- Group B consists of acid dyes with lower levelling power, higher substantivity and high wet fastness on polyamide.

Many of these acid dyes with inferior levelling power reveal clear differences in fibre structure (so-called streakiness), so that it is usually necessary to add levelling and retarding agents.

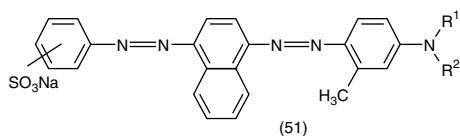
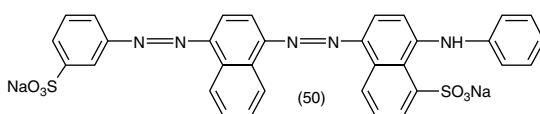
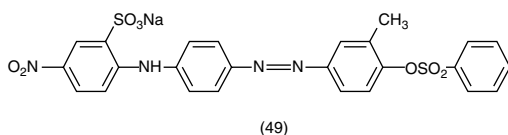
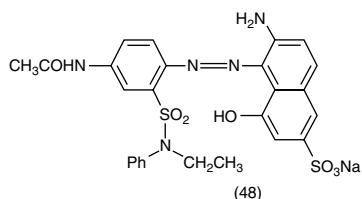
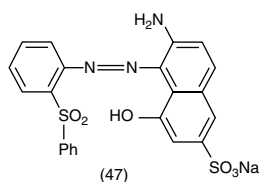
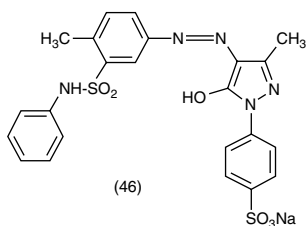
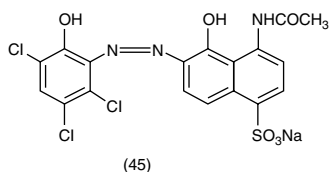
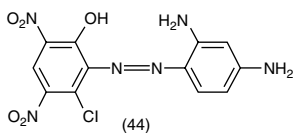
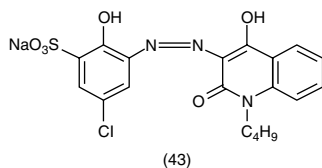


### 15.5 Monoazo metal-complex dyes.

A few representative structures of Group A are C.I. Acid Yellow 25, C.I. 18835 [6359-85-9] (46), C.I. Acid Red 42, C.I. 17070 [6245-60-9] (47) and C.I. Acid Red 32, C.I. 17065 [6360-107] (48). The main application of Group A dyes are in carpet dyeing.

Some of the Group B dyes are C.I. Direct Yellow 65, C.I. 14170 [6408-98-8] (49) and C.I. Acid Blue 113, C.I. 26360 [3351-05-1] (50). They are used exclusively for clothing textiles, for which stringent requirements are placed on wet fastness. Some secondary disazo dyes such as 51 and 1:2 metal-complex dyes are gaining importance in the dyeing of synthetic polyamides.





### 15.6 Monoazo acid dyes with enhanced light fastness.

The chemometric approach has been employed in the structure optimisation in a series of acid dyes for wool, and synthetic polyamides (Carpignano *et al.*, 1985; De Giorgi and Carpignano, 1996; De Giorgi *et al.*, 1997).

## 15.4 Anthraquinone dyes

Anthraquinone acid dyes are rich in violet through blue to green complementing the azo dyes. They have very good light fastness. They may be subdivided into the following types.

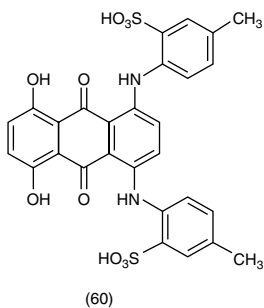
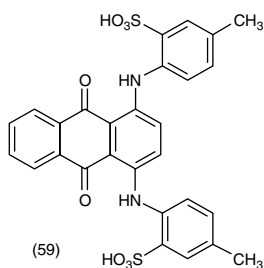
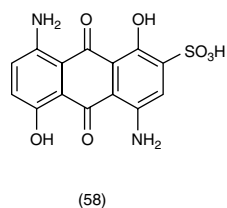
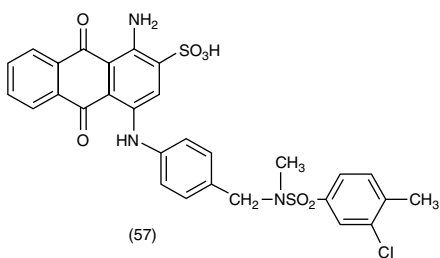
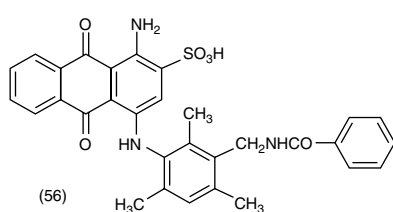
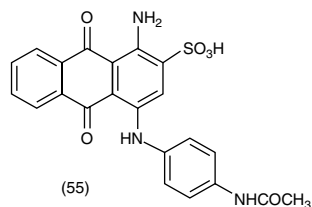
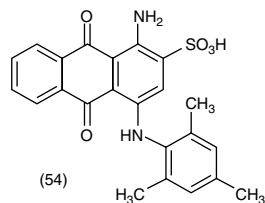
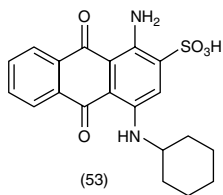
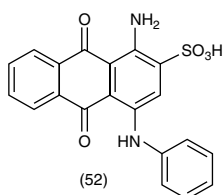
1. 1-Amino-4-(substituted)amino anthraquinone-2-sulphonic acids
2. Diamino dihydroxy anthraquinone sulphonic acids
3. 1,4-Diaminoanthraquinones with external sulphonic acids
4. 1-Amino-4-hydroxy anthraquinones with external sulphonic acid groups
5. Other acid anthraquinone dyes.

Anthraquinone acid dyes offer bright blue shades not obtainable in azo dyes. The red and yellow anthraquinone dyes are of little importance. Green dyes obtained by the combination of yellow and blue dyes have mostly inferior wash fastness. The uniformly dyeing green dyes of the anthraquinone series have proved their special value in this context. When synthetic polyamides were known some selected dyes from this series were used. Special acid dyes of this class have been recently developed for this purpose.

#### 15.4.1 1-Amino-4-(substituted)amino anthraquinone-2-sulphonic acids

These are obtained by the condensation of bromamine acid with aromatic or cycloaliphatic amines, by an Ullmann reaction catalysed by copper or copper salts. This group of blue acid dyes has important usage value and there are several reported commercial structures (Chengqin, 1979; Chunlong, 1989, p. 189; Foris, 1977, p. 229; p. 57; Mengzheng, 1984; Venkataraman, 1952; Zollinger, 1987, p. 169). The shade, levelling characteristics and light fastness can be varied over a wide range by selecting particular amines. Cycloaliphatic amines give the same brightness as aliphatic amines but give greater light fastness. Arylamines substituted with alkyl, halogen, aryl, aryloxy or sulphonic ester group provide dyes with better wash fastness and affinity in neutral media but levelling is improved. The brilliance is increased by the substituents at the o-position accompanied by hypsochromic shift. The influence of methyl groups on the colour and dyeing characteristics of acid dyes derived from 1-amino-4-bromoanthraquinone-2-sulphonic acid and arylamines has been studied (Zhang and Hou, 1996). A new method for the preparation of bromamine acid directly from bromamine acid has been reported (Ghaieni *et al.*, 2007). A convenient and efficient process for the manufacture of C.I. Acid Blue 78 from anthraquinone has been reported (Ghaieni *et al.*, 2008).

Some examples are C.I. Acid Blue 25, C.I. 62055 [6408-78-2] (52), C.I. Acid Blue 62, C.I. 62045 [4368-56-3] (53), C.I. Acid Blue 129, C.I. 62058 [6397-02-0] (54), C.I. Acid Blue 40, C.I. 62124 [6424-85-7] (55), and 56, and 57.



### 15.7 Anthraquinone acid dyes.

#### 15.4.2 1-Amino-2-aryloxy-4-(substituted)amino anthraquinones

These are the violet acid dyes with a brilliant hue and excellent fastness introduced between 1960 and 1970 (Peter and Gunthart 1951; Swiss Patent, 1966). The violet acid dyes of the copper complex azo type gives dull shades while those of the triphenylmethane type have very poor light fastness. The

anthraquinone violet dyes of this type can be used for dyeing natural and synthetic polyamide fibres in bright shades of high light fastness.

They are obtained by condensation of bromamine acid with a di- or tri-alkylaniline and subsequent condensation with an alkylphenol followed by sulphonation. While the general formula of such dyes is known, the exact number of sulphonic acid groups and their orientation are not clearly elucidated (Ciba-Geigy, 1980; Sandoz, 1979; Schwander *et al.*, 1970). The structure and dyeing properties of such anthraquinone violet acid have been reported (Zhang *et al.*, 1997).

#### 15.4.3 Diamino dihydroxy anthraquinone sulphonic acids

These are the oldest synthetic dyes for wool, but their importance has decreased considerably. An example is C.I. Acid Blue 43, C.I. 63000 [2150-60-9] (58).

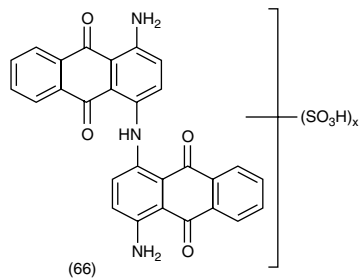
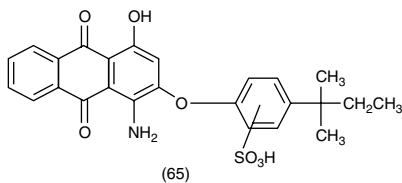
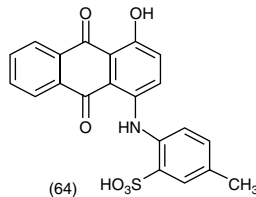
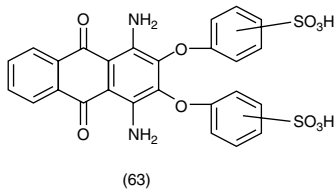
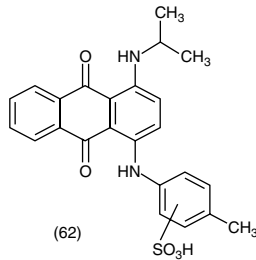
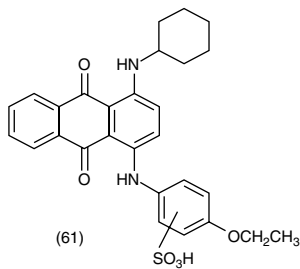
#### 15.4.4 1,4-Diaminoanthraquinones with external sulphonic acid groups

These are obtained by sulphonation of the corresponding dye base derived from quinizarin or halo amino anthraquinones. The reaction products of quinizarin with aromatic or araliphatic amines predominate in number and importance. The introduction of hydroxy function into the 5- or the 5,8 positions causes the expected red shift. Substituents influence the wash fastness and levelling. The shade can be varied from brilliant blue to green by appropriate amines. Sterically hindered amines, araliphatic and cycloaliphatic amines lead to brilliant blue shades. Dyes in this series exhibit more light fastness than the derivatives of bromamine acid. Among the unsymmetrically substituted dyes derived from 1-amino or 1-alkylamino-4-haloaminoanthraquinones, 1-alkylamino anthraquinones have inferior light fastness. Exceptions are the 1-sec-alkylamino-4-halo anthraquinones. Introduction of alkoxy or aryloxy groups into the 2 position introduces a blue shift giving bright violet dyes.

Examples are C.I. Acid Green 25, C.I. 61570 [4403-90-1] (59), C.I. Acid Green 41, C.I. 62560 [4430-16-4] (60), greenish blue dyes 61, 62 and C.I. Acid Violet 42, C.I. 62026 [64026 [6408-73-7] (63).

#### 15.4.5 1-Amino-4-hydroxy anthraquinones with external sulphonic acid groups

These are obtained by the partial reaction of quinizarin with arylamines, followed by sulphonation. They are the violet level dyeing ones. Derivatives of 1-amino-4-hydroxy-2-phenoxy anthraquinones were developed for polyamides of synthetic origin.



### 15.8 Anthraquinone acid dyes.

Examples are C.I. Acid Violet 43, C.I. 60730 [4430-18-6] (64) and the bluish brilliant red dye 65.

#### 15.4.6 Other acid anthraquinone dyes

In addition to the classes mentioned above a whole series of specially developed dyes are available. For example, derivatives of the anthrimide and carbazole series are known to be very light-fast grey and brown wool dyes. The sulphonation products of 1,5- and 1,8-diarylamino anthraquinones are violet dyes commonly used as mixtures.

An example is C.I. Acid Black 48, C.I. 65005 [1328-24-1] (66).

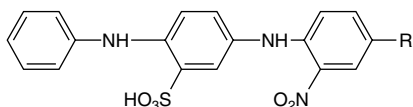
A novel azo-anthraquinone dye made through innovative enzymatic process has been the subject of a recent publication (Enaud *et al.*, 2010).

## 15.5 Acid nitro dyes

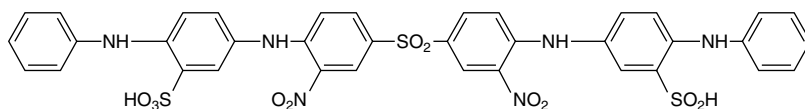
These were first used in the colouration of wool. More recently, like the acid azo nitro dyes, they have been used for the dyeing of synthetic polyamides. They have low colour strength but higher light fastness.

The earliest anionic nitro dyes were produced by treating picryl chloride with aromatic amino sulphonic acids. However, the dye 67A [15347-52-1] obtained by the reaction of 2,4-dinitro chlorobenzene with 4-amino diphenylamine-2-sulphonic acid became industrially important. The dye 67A gives light-fast yellow shades on wool and synthetic polyamide fibres. Relationships between the structure of nitrodiphenylamine derived mono-azo acid dyes and their spectroscopic and fastness properties have been established (Szadowski and Przybylski, 1984).

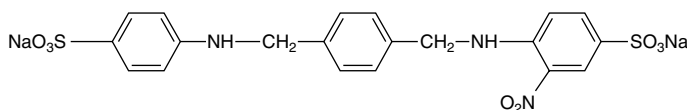
A mixture of the dyes 67 [72829-30-2] and 68 [72829-29-9] is commercially available as Nylosan Yellow Brown EGL (Sandoz). The dyes with sulpho-nate ester group 69 and many other functionally substituted derivatives are known. C.I. Acid Brown 13, C.I. 10410 (70) is a bifunctional acid nitro dye produced by the reaction of 4,4'-dichloro-3,3'-dinitrodiphenyl sulphone with 4-aminodiphenylamine-4-sulphonic acid. The dye 71 gives brilliant yellow colour on synthetic polyamide. In this dye the conjugation is interrupted by the methylene bridges.



- (67) R = SO<sub>2</sub>NH<sub>2</sub>  
 (67A) R = NO<sub>2</sub>  
 (68) R = SO<sub>2</sub>NHPh  
 (69) R = SO<sub>2</sub>OAlkyl



(70)



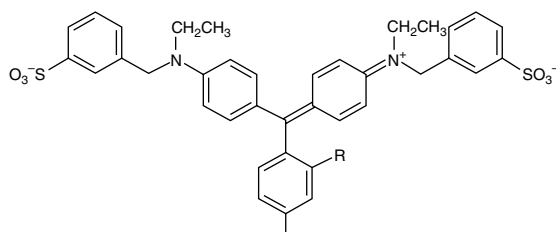
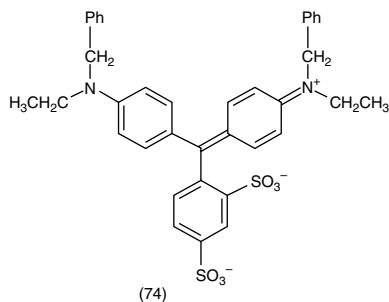
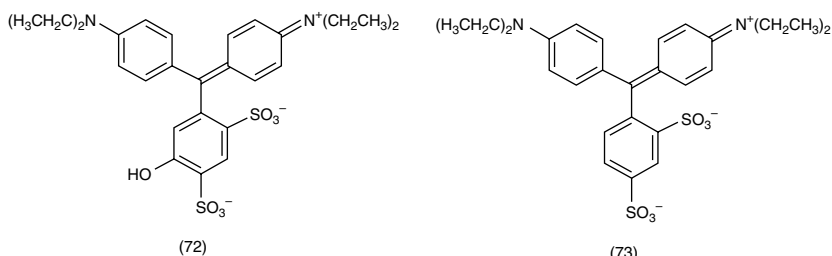
(71)

### 15.9 Nitrodiphenylamine acid dyes.

## 15.6 Triphenylmethane acid dyes

Acid dyes with triphenylmethane (blues and greens) and xanthenes (reds and violets) chromophores are less important though they are very brilliant. They have poor light fastness.

Triphenylmethane acid dyes were initially synthesised by sulphonation of the parent cationic dyes. Alcohol soluble aniline blue was converted by Nicholson in 1862 into a soluble form suitable for dyeing. Acid triphenylmethane dyes from benzylated aniline were found to be good wool dyes. Introducing a sulphonic acid group ortho to the methane carbon was found to have improved the alkali fastness. The first dye of this type was Patent

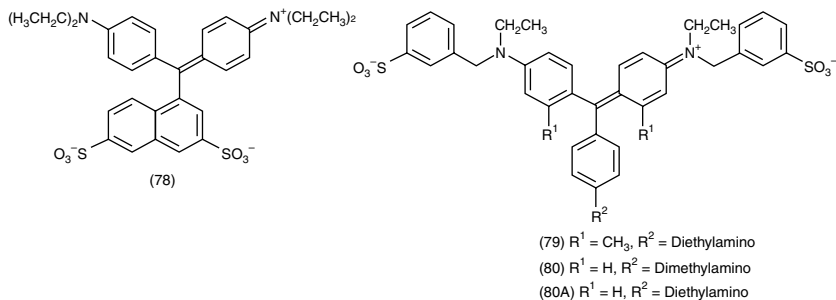


(75)  $\text{R} = \text{SO}_3\text{H}$

(76)  $\text{R} = \text{H}$

(77)  $\text{R} = \text{Cl}$

### 15.10 Triarylmethane acid dyes.



### 15.11 Triarylmethane acid dyes.

Blue V obtained by Hermann in 1888 by sulphonation of the dye obtained from 3-hydroxy benzaldehyde with diethyl aniline.

Patent Blue V, C.I. Acid Blue 3 [3536-49-0] (72) is a valuable dye for wool. A similar good dye is Patent Blue VE, C.I. Acid Blue 1, C.I. 42045 [129-17-9] (73), which does not contain a hydroxy group. If diethyl aniline is replaced by ethyl benzyl aniline in the synthesis of Patent Blue VE, Patent Blue AF, C.I. Acid Blue 7, C.I. 42080 (74) is obtained.

Derivatives of N-ethyl-N-(3-sulphobenzoyl) aniline are also important dyes in this series. Examples are C.I. Acid Blue 9 (Patent Blue AE, C.I. Food Blue 2, C.I. 42090) [3844-45-9] (75), C.I. Acid Green 3 (C.I. Food Green 1, C.I. 42085) [4680-78-8] (76) and C.I. Acid Green 9, C.I. 42100 [4857-81-2] (77).

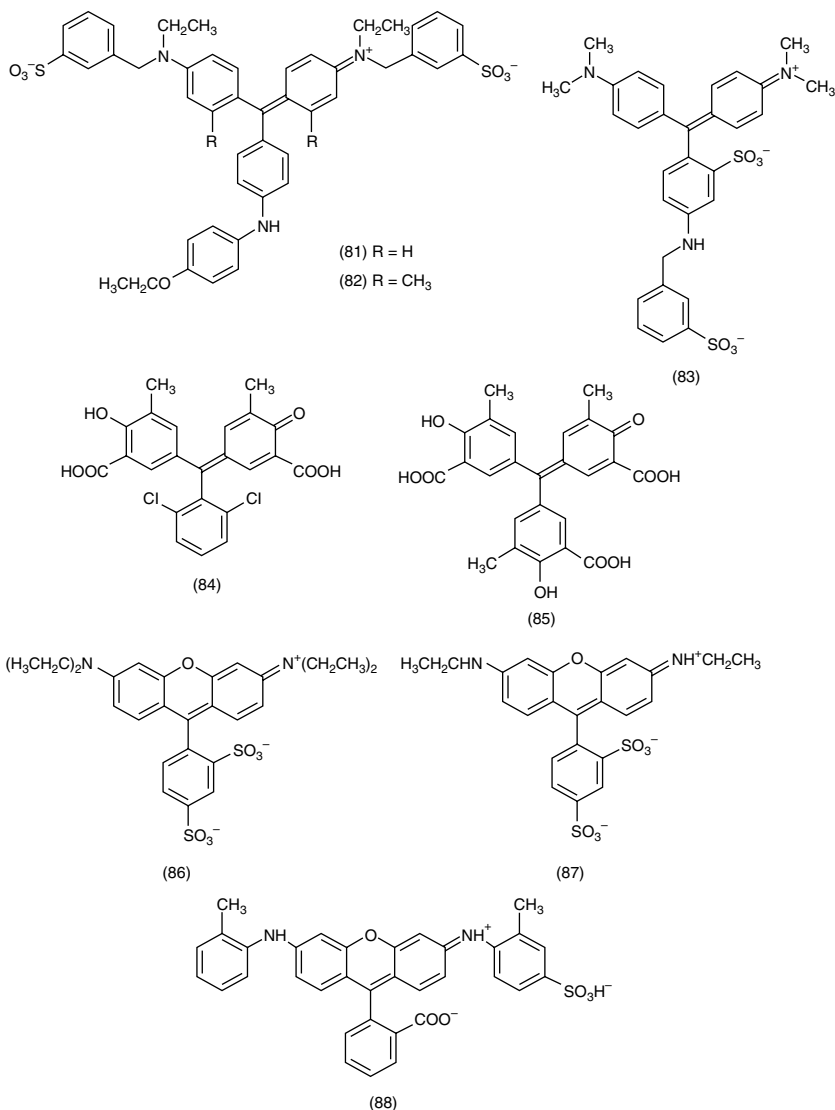
Derivatives of naphthalene sulphonic acids are also found in this range. An example is C.I. acid Green 16, C.I. 44025 (78), which is prepared by the condensation of 4,4'-bis(diethyl amino)benzhydrol with 2,7-naphthalene disulphonic acid, and oxidation of the leuco compound.

Arylated pararosanine dyes with one sulphonic acid group are water-insoluble betaines and have pigment character. The more highly sulphonated triphenyl pararosanines are readily water-soluble acid dyes and find application in printing inks. Examples are C.I. Acid Blue 93, C.I. 42780; C.I. Acid Blue 104, C.I. 42735 (79); C.I. Acid Blue 49, C.I. 42640 [1694-09-3] (80); C.I. Acid Violet 17, C.I. Food Violet 1, C.I. 42650 [4129-84-4] (80A); C.I. Acid Blue 90, C.I. 42655 [6104-58-1] (82) and C.I. Acid Blue 13, C.I. 42571 (83).

Hydroxy triarylmethane dyes with an adjacent carboxylic acid group find application as mordant dyes. Examples are C.I. Mordant Blue 1, C.I. 43830 (84) and C.I. Mordant Violet 16, C.I. 43865 (85).

Acid dyes of the rhodamine class are used more as laser dyes. Examples are Sulphorhodamine B, C.I. Acid Red 52, C.I. 45100 [3520-42-1] (86),

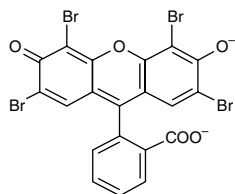




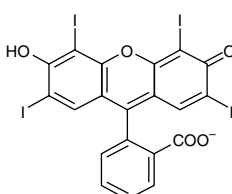
### 15.12 Pyronine acid dyes.

Sulphorhodamine G, C.I. Acid Red 50 (87) and Fast Violet ARR, C.I. Acid Violet 9, C.I. 45190 (88).

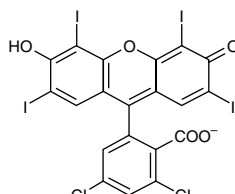
Heterocyclic analogues or triarylmethane dyes like diazines are also converted into acid dyes. An example of an acid safranin dye is Acid Cyanine BF, C.I. 50230 [6448-97-1] (93); Indulines 6B (94); Wool Fast



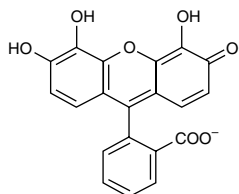
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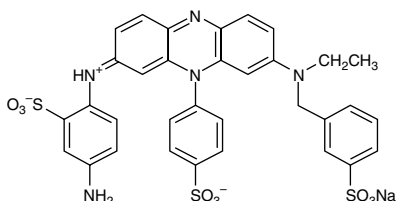
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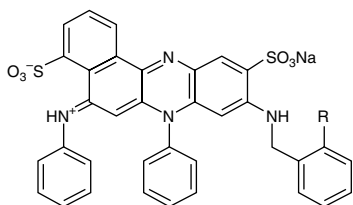
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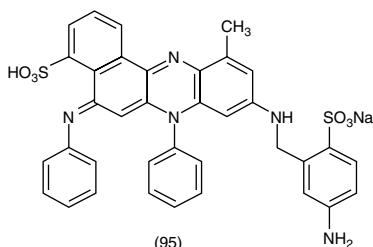
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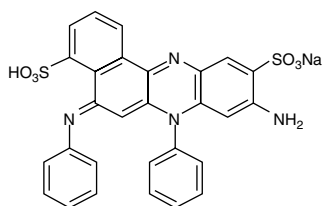
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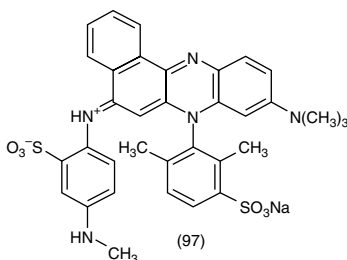
(94)



(95)



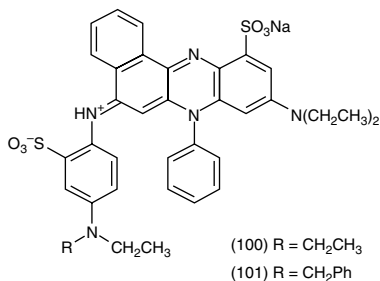
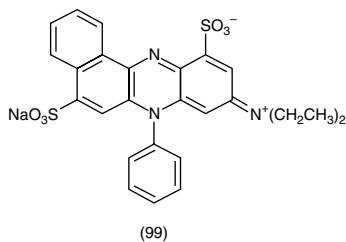
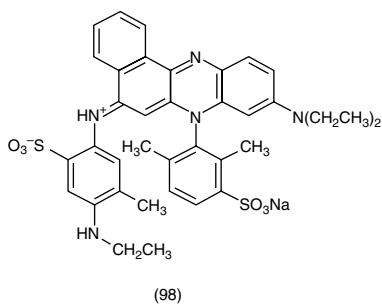
(96)



(97)

### 15.13 Pyronine and diazine acid dyes.

Blue FFG, C.I. 50330 [6837-47-4] (94); Acilian Fast Violet FB or Wool Fast Violet B, C.I. 50325 (95); Supranol Fast Cyanine B, C.I. 50335 [6378-89-8] (96); Fast Blue EB, C.I. 50300 [6471-74-5] (97); Supranol EG, C.I. 50310 [6378-87-6] (98); Supranol Blue EG (99); Novazol Acid Blue GL (100) and Polar Blue G (101).



#### 15.14 Diazine acid dyes.

### 15.7 Water-repellent dyes

Water repellence is an important property required for comfort wear. For comfort wear it is necessary for the fabric to be sufficiently porous to allow moist air to circulate. Water-repellent finish is given to fabric by way of finishes which form a water-repellent layer on the surface of the material without filling up the interstices. Several fluorine containing acid dyes are known in the literature (Chao *et al.*, 1998; Hamada *et al.*, 1989, 1990, 1991, 1993) and recently dyes having inherent water-repellent characteristics have been prepared (Chao *et al.*, 1998; Sekar and Rajule, 2004; Teli *et al.*, 2007).

### 15.8 Acid dyes with inherent light fastness

Acid dyes with improved light fastness have become important particularly in connection with the usage of acid dyes in information recording systems. The inferior light fastness may be due to several reasons. Auto oxidation reaction of dyes is generally considered to occur on exposure to ultraviolet (UV) radiation and prevented by the addition of UV absorbers or anti-oxidants such as hindered phenols or naphthylamines. In recent years as an approach to the photostabilisation of dyes attempts have been made to

prepare dyes with built-in photostabilising moiety (Oda, 2001; Rajagopal and Seshadri, 1988).

### 15.9 Acid dyes free from 1-naphthylamine

1-Naphthylamine has long been established as a diazo component and an intermediate component in dyes of the type: amine → intermediate component → coupler, giving heavy shades on wool and cotton.

Even though these dyes are known for their brilliance and fastness properties, the pronounced carcinogenicity of 1-naphthylamine may restrict the use of such dyes in the future. Interest has therefore developed in recent years in the replacement of toxic diamines and amines (Freeman *et al.*, 1989, 1991). In this connection 3-acetamidoaniline derivatives with selected substituents at 4 position have been suggested as suitable substitutes (Hughes and Lambie, 1981; Mischke and Schlafer, 1987; Polish Patent 124170, 1984; Schlafer and Springer, 1985; Sumitomo, 1985; Tzikas, 1988). Several mono-azo and disazo dyes have been prepared in these lines and they have been compared with their 1-naphthylamine counterparts (Sekar, 1995, 1996; Sekar and Nayar, 2006).

### 15.10 Future trends

Developments in the basic chromogenic systems seem to be more or less saturated. However, functions other than imparting colour are being closely researched. There are publications discussing acid dyes with additional functions such as water repellency, inbuilt UV-absorbing units and antibacterial properties. These kinds of dyes are envisaged to eliminate the additional finishing steps such as water-repellent finish, antibacterial finish and other finishing treatments. It is likely that commercial dyes will evolve in these lines.

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**Abstract:** There is considerable awareness among the consumers for environmental-friendly textiles. Stringent environment protection regulations exist in most of the countries. The environmental pollution is more noticeable during chemical processing operations of textiles, particularly dyeing. The present chapter critically reviews the environmental issues associated with each dye class and the dyeing processes. The chapter is divided into three broad sections, namely, classification of dyes, environmental issues associated with different dye classes and the environmental-friendly dyeing processes. Among the different dye classes, dyes based on azo structure are found to be associated with human toxicity; as a result there is a ban on several azo dyes based on harmful amines, and these dyes have been withdrawn from the market. The human toxic effects of some of the dyes include respiratory problems, skin sensitization and, in extreme cases, carcinogenicity. Few options have been suggested to modify the intermediate/dye structure to overcome the human toxicity problems associated with identified toxic dyes. The section on environmental-friendly dyeing processes reviews the environmental problems associated with dyeing of reactive, vat, sulphur dyes on cotton; chrome dyes on wool and carrier dyeing of disperse dyes on polyester. In the concluding section, some of the future trends are enlisted. These trends include development of new-generation dyes based on the use of safer intermediates, while maintaining desirable tinctorial, cost and fastness properties. This new generation of dyes should require fewer dyeing assistants, especially salt, retarders and accelerants. There is a need for better disclosure of chemical constitution of new-generation dyes and specialties auxiliary products. It is pointed out that lack of information on chemical structures of dyes and speciality products will make evaluation of pollution problems, substitutions, and so forth more difficult in the future. The introduction of systems like REACH and GHS should be helpful in this respect.

**Key words:** environment, dyes, toxicity, carcinogen, hazardous potential

## 16.1 Introduction

The first synthetic textile colourant was produced in 1856 by William Perkin by oxidation of aniline. By the early 1880s, diazotisation was a known reaction, and chemists like Greiss, Walter and Boettiger attempted to synthesise commercially useful dyes.<sup>1</sup> During the ensuing century of dye development, thousands of synthetic dyes and pigments have been produced and used commercially. Presently, the world production of

colourants is approximately 1 million tonnes per year, of which about 50% are textile dyes.<sup>2</sup>

The workers involved in the manufacture of dyes became exposed not only to the dyes themselves but also to the chemical intermediates used in their manufacture. Many years later, it became apparent that workers involved in the manufacture of certain dyes, and particularly dyes based on benzidine and 2-naphthylamine, developed a high incidence of bladder cancer.<sup>3</sup> It was established later that both benzidine and 2-naphthylamine are indeed human bladder carcinogens. Once this information was known, all responsible dye manufacturers took action to cease production of these proven human carcinogens and any dyes using these dye intermediates. It is to its credit that the colourant manufacturing industry of Western Europe began to investigate the toxicological and eco-toxicological properties of dyes and pigments long before chemical and environmental regulations existed. Thus, in 1974, the member companies of ETAD (Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers) voluntarily developed Safety Data Sheets with appropriate information on the hazardous potential of colourants. Nowadays, the concept of Safety Data Sheets has spread worldwide.<sup>3</sup> The EU Commission has proposed a new regulatory framework for the Registration, Evaluation and Authorisation of Chemicals (REACH). The aim is to improve the protection of human health and the environment through better and earlier identification of the properties of chemical substances.<sup>4</sup> The Globally Harmonized System of Classifying and Labelling Chemicals (GHS), is voluntary, but it was agreed at the 2002 UN World Summit on Sustainable Development in Johannesburg that the GHS should be implemented worldwide, with a target date of 2008. The GHS will provide harmonised health and safety information for chemical substances and mixtures.<sup>5</sup>

Currently, the three main regulatory bodies worldwide are the European Inventory of Existing Commercial Substances (EINECS),<sup>6</sup> the Toxic Substances Control Act (TSCA) in the USA,<sup>7</sup> and the Ministry of Technology and Industry (MITI) in Japan.<sup>8</sup> Many countries have also developed their own environmental standards for pollution prevention.

On the one hand textile dyes should be safe for human beings; on the other hand they should also be safe for the environment during the use and after the Colouration of textiles. Traditionally, dye manufacturers' goals have been to produce low-cost dyes with high tinctorial value, brilliance, ease of application and good fastness properties. Although safety has, over time, become a major consideration in the synthesis of dyes from intermediates, their removal during effluent treatment has not been a significant consideration in dye design.

The present chapter gives a brief classification of dyes and reviews critically the human and environmental toxicity of dyes, dyeing chemicals and auxiliaries and also the environmentally friendly dyeing processes. A note on future trends on dye research and dyeing processes is also included.

## 16.2 Classification of dyes

Textile dyes can be classified according to their chemical composition or according to their application class. The *Colour Index* (C.I.) published jointly by the Society of Dyers and Colourists (UK) and by the American Association of Textile Chemists and Colorists (USA) is the most extensive compendium of dyes and pigments including 12 000 products under 2000 C.I. generic names classified according to their chemical composition. Publication of new dyes and their classification have gradually diminished essentially due to reasons of intellectual property right.<sup>9</sup> At the industrial level the classification according to application class is preferred.<sup>10</sup>

Table 16.1 lists the major dye classes, the types of fibres for which they have an affinity and type of pollutants associated with dyeing processes.<sup>11</sup>

### 16.2.1 Acid dyes

Chemically acid dyes are based on azo, anthraquinone, triphenylmethane Cu-phthalocyanin chromophoric systems which are water soluble due to presence of up to four sulphonic acid groups. These dyes are applied mainly to polyamide and wool. They are also used for silk and some modified acrylic fibres. Acid dyes exhibit little affinity for cellulose and polyester fibre. The most common chemicals and auxiliaries used during dyeing with acid dyes are as follows:

- Sodium sulphate, sodium acetate and ammonium sulphate.
- pH regulators: acetic, formic and sulphuric acid, but also ammonium salts and phosphoric acid salts.
- Levelling agents, mainly cationic compounds such as ethoxylated fatty amines.
- After-treatment agents such as formaldehyde condensates with aromatic sulphonic acids.

Acid dyes are non-toxic except two dyes – C.I. Acid Orange 150 and 165 – which have been classified as toxic by ETAD. C.I. Acid Violet 17 is reported to have an allergenic effect. Presence of acid dyes in the effluent is low because of high degree of exhaustion and fixation.

### 16.2.2 Basic (cationic) dyes

Cationic dyes contain a quaternary amino group which can be an integral part of the conjugated system. Sometimes a positively charged atom of oxygen or sulphur can be found instead of nitrogen. Cationic dyestuffs are exclusively used for dyeing acrylic fibres, modified polyamide and polyester fibres, and blends. Cationic dyes are strongly bound to the fibre by electrostatic attraction and do not migrate easily. In order to achieve level dyeing,

**Table 16.1** Dye classes, their characteristics and pollutants associated with the dyeing process<sup>11</sup>

Dye class	Characteristics	Fibre suitability	Typical fixation (%)	Pollutants associated
Acid	Water-soluble anionic compounds	Wool, nylon, silk	80–93	Colour, organic acids, dyeing auxiliaries
Basic	Water soluble, applied from weakly acid bath, very bright shades	Acrylic, modified polyester	97–98	Colour, organic acids, dyeing auxiliaries
Direct	Water soluble, anionic compounds, low wash fastness	Cotton, other cellulose, wool, silk	70–95	Colour, salt, dye fixing agents
Disperse	Water insoluble, low mol. wt.	Polyester, acetate other synthetics	80–92	Colour, organic acids, dispersing agents, carriers
Reactive	Water soluble, covalent bond with fibre, popular dye class	Cotton, other cellulose, wool, silk, nylon	60–90	Colour, salt, alkali, soaping agents
Sulphur	Sulphur containing organic compounds, water insoluble, solubilised on weak alkaline reduction	Cotton, other cellulose	60–70	Colour, sodium sulphide, alkali, oxidising agent
Vat	Water insoluble, chemically complex, solubilised on strong alkaline reduction	Cotton, other cellulose	80–95	Colour, sodium hydrosulphite, alkali, soaping agent
Azoic	<i>In situ</i> colour formation by coupling reaction	Cotton, other cellulose	–	Alkali, unfixed colour, naphthol, diazotised base, soaping agent
Pigment	Water insoluble, no fibre affinity, fixation with the help of binder	Cotton, cotton/PET blends	100	Colour, binder, polymerising catalyst

Source: Adapted from EPA, USA, 1995, Snowden; Swan L J, *Pollution Prevention in Textile Industries in Industrial Pollution Prevention Handbook* (Ed. H M Freeman), McGraw-Hill, Inc, New York, (1995).

specific levelling auxiliaries (called retarders) are normally employed. The most important group of retarders is represented by quaternary ammonium compounds with long alkyl side-chains (cationic retarders). Electrolytes and anionic condensation products between formaldehyde and naphthalene sulphonic acid may also be found.

Many cationic dyes exhibit high aquatic toxicity but, when applied properly, they show dye fixation close to 100%. Problems are more often attributable to improper handling procedures, spill cleanup and other upsets. The following dyestuffs have been classified as toxic by ETAD: C.I. Basic Blue 3, 7, 81, Basic Red 12, Basic Violet 16 Basic Yellow 21.

### 16.2.3 Direct (substantive) dyes

Direct dyes (also called substantive dyes) can be azo compounds, stilbenes, oxazines or phthalocyanines. They always contain solubilising groups (mainly sulphonic acid groups, but carboxy and hydroxyl groups can also be found). Direct dyes are used for dyeing of cotton, rayon, linen, jute, silk and polyamide fibres.

The following chemicals and auxiliaries are used for satisfactory dyeing:

- Electrolytes, usually sodium chloride or sodium sulphate: to suppress the negative surface potential of fibre and to assist the dye exhaustion. The electrolytes also favour the aggregation of dye ions on the fibre.
- After-treatment agents: used to improve wet fastness properties. They are usually quaternary ammonium compounds with long hydrocarbon chains. Formaldehyde condensation products with amines, cyanamide or dicyandiamide and polynuclear aromatic phenols, may also be used for this purpose.

The main emphasis of research for direct dyes has been the replacement of carcinogenic benzidine dyes.<sup>12</sup> C.I. Direct Orange 62 has been classified as toxic by ETAD.

### 16.2.4 Disperse dyes

Disperse dyes are characterised by the absence of solubilising groups and low molecular weight. From a chemical point of view more than 50% of disperse dyes are simple azo compounds, about 25% are anthraquinones and the rest are methine, nitro or naphthoquinone dyes. Disperse dyes are used mainly for polyester, but also for cellulose acetate and triacetate, polyamide and acrylic fibres. Disperse dyes are supplied as powder and liquid products. Powder dyes contain 40–60% of dispersing agents, while in liquid

formulations the content of these substances is in the range of 10–30%. Formaldehyde condensation products and lignin sulphonates are widely used for this purpose. The following chemicals and auxiliaries are used for dyeing with disperse dyes;

- Dispersants: although all disperse dyes already have a high content of dispersants, they are further added to the dyeing liquor and in the final washing step.
- Carriers: for polyester fibre, dyeing with disperse dyes at temperatures up to 100°C requires the use of carriers. Because of environmental problems associated with the use of carriers, polyester is preferably dyed under pressure at temperature >100°C without carriers. However, carrier dyeing is still important for polyester-wool blends.
- Thickeners: polyacrylates or alginates are usually added to the dye liquor in padding processes.
- Reducing agents (mainly sodium hydrosulphite) are added in solution with alkali in the final washing step for the removal of unfixed surface dye.

Owing to their low water solubility, disperse dyes are largely eliminated by adsorption on activated sludge in waste water treatment plants. Some disperse dyes contain organic halogen, but they are not expected to be found in the effluent after waste water treatment because of their adsorption on activated sludge.

The following disperse dyes potentially have an allergenic effect:

- C.I. Disperse Red 1, 11, 15, 17
- Disperse Blue 1, 3, 7, 26, 35, 102, 124
- Disperse Orange 1, 3, 76
- Disperse Yellow 1, 9, 39, 49, 54, 64.

Conventional dispersants (formaldehyde condensation compounds, ligno-sulphonates, etc.) are poorly biodegradable. However, some dyes are formulated with more readily bio-eliminable dispersants.

### 16.2.5 Metal-complex dyes

Metal-complex dyes (also called premetallised dyes) may be broadly divided into two classes: 1:1 metal complexes and 1:2 metal complexes. The dye molecule will be typically a monoazo structure containing additional groups such as hydroxyl, carboxyl or amino groups, which are capable of forming strong coordination complexes with transition metal ions. Typically, chromium, cobalt, nickel and copper are used. Metal-complex dyes have good affinity for protein fibres. 1:2 metal-complex dyes are also suitable for

polyamide fibres. Dyeing with metal-complex dyes requires the use of the following chemicals and auxiliaries:

- pH regulators – sulphuric, formic, acetic acid
- Electrolytes – sodium sulphate, ammonium acetate and sulphate
- Levelling agents – mixtures of anionic and non-ionic surfactants.

Bio-eliminability of dyes can be <50%. Some dyes contain organic halogens (adsorbable organic halogen – AOX) in waste water, which depends on the bio-eliminability of the dyes concerned.

Metals can be found in the effluent due to unfixed dye. However, Cr III and the other transition metals used in metal-complex dyes are an integral part of the chromophore.<sup>13</sup>

### 16.2.6 Mordant (chrome) dyes

This class of dye is classified as Mordant dyes in *Colour Index*, but chromium has become the almost universally used mordant and the class is commonly referred to as chrome dyes. From a chemical point of view they can be regarded as acid dyestuffs that contain suitable functional groups capable of forming metal complexes with chrome. They do not contain chrome in their molecule, which instead is added as dichromate, or chromate salt during or after dyeing to allow dye fixation. Mordant dyestuffs are generally used for protein (wool and silk) fibres. The following chemicals and auxiliaries are used during dyeing;

- Potassium dichromate or chromate
- Formic or acetic acid as pH regulators
- Other organic acids such as tartaric and lactic acid, used to enhance the degree of conversion of Cr VI to Cr III
- Sodium or ammonium sulphate.

The major environmental issues are human toxicity during handling and the contamination of the effluent by toxic chromium salts used after dyeing.

### 16.2.7 Azoic (naphthol) dyes

The insoluble dye is synthesised directly in the fibre as the result of the coupling reaction between a diazotised base (developing agent) and a naphthol (coupling component). These dyes are mainly used for cellulosic fibres, particularly cotton. The coupling components, usually known as naphthols, are derivatives of the anilides of the 2-hydroxy-3-naphthoic acid. Developing agents are diazotisable amines or diamines or substituted anilines, toluidines, anisidines, azobenzenes or diphenylamines. Some of these amines and

in particular, p-nitroaniline, p-chloroaniline and  $\beta$ -naphthylamine are on the priority list of harmful chemicals and their use is forbidden.

### 16.2.8 Reactive dyes

Reactive dyes are mainly used for dyeing cellulose fibres such as cotton and viscose, but they are also increasingly gaining importance for wool and polyamide. The range of available reactive dyes is wide and enables a large number of dyeing techniques to be used. In dyeing cellulose fibres with reactive dyes the following chemicals and auxiliaries are used:

- Alkali (sodium carbonate, bicarbonate and caustic soda)
- Salt (mainly sodium chloride and sulphate)
- Urea may be added to the padding liquor in continuous processes
- Sodium silicate may be added in the cold pad-batch method.

Poor dye fixation has been a long-standing problem with reactive dyes in particular in batch dyeing of cellulose fibres, where a significant amount of salt is normally added to improve dye exhaustion (and therefore also dye fixation). Thus colour and salt in the effluent are major environmental issues in reactive dyes. Because both unfixed reactive dye and its hydrolysed form are water soluble, they are difficult to eliminate in biological waste water treatment plants. Many reactive dyes contain halogens. However, since it is not attached to the chromophore, reactive dyes are considered to be free from AOX issues.

Heavy metals can be present both as impurities from the production process (limits have been set by ETAD) and as an integral part of chromophores. The latter concerns phthalocyanine dyes which are still widely used specifically for blues and turquoise shades.

### 16.2.9 Sulphur dyes

Sulphur dyes are made up of high molecular weight compounds, obtained by reaction of sulphur or sulphide with amines and phenols. The exact chemical structure is not always known because these are mixtures of molecules of a high level of complexity. Sulphur dyes are insoluble in water, but after reduction under alkaline conditions they are converted into the leuco form, which is water soluble and has high affinity for the fibre. After absorption into the fibre they are oxidised and converted to the original insoluble state.

Sulphur dyes are mainly used for cotton and viscose. They may also be used for dyeing cellulose in synthetic fibre blends including polyamides and polyesters. Sulphur black is most popular to produce low-cost black shades.

Sodium sulphide and sodium hydrogen sulphide are generally employed as reducing agents. In all processes the dye is finally fixed on the substrate



by oxidation. Hydrogen peroxide or halogen-containing compounds such as bromate, iodate and chlorite are the most commonly used oxidising agents.

Apart from the above-mentioned reducing and oxidising agents, additional chemicals and auxiliaries required when dyeing with sulphur dyes are as follows:

- Alkali (mainly sodium carbonate or caustic soda)
- Salt (sodium chloride and sulphate)
- Dispersing agent: usually they are naphthalene sulphonic acid-formaldehyde condensates, lignin sulphonates and sulphonated oils
- Complexing agents: ethylenediaminetetraacetic acid (EDTA) and polyphosphates are used in some cases to prevent negative effects due to the presence of alkaline-earth metal ions.

Sulphur dyes are water insoluble after oxidation and therefore they can be largely eliminated by adsorption on the activated sludge in waste water treatment plants.

Poorly biodegradable dispersants are present. New formaldehyde condensation products with higher bio-elimination (>70%) are now available.

### 16.2.10 Vat dyes

From a chemical point of view, vat dyes can be divided into two groups: indigoid vat dyes and anthraquinoid vat dyes.

Like sulphur dyes, vat dyes are insoluble in water, but they become water soluble and substantive for the fibre after reduction in alkaline conditions (vatting). They are then converted again to the original insoluble form by oxidation and in this way they remain fixed into the fibre. Vat dyes are used most often in dyeing of cotton and other cellulose fibres. They can also be applied for dyeing of blends containing cellulose fibres.

Various reducing agents are used. Sodium dithionite (sodium hydrosulphite) is still the most widely employed, although it has some limitations.

The following chemicals and auxiliaries may be found in dyeing processes:

- Sodium hydrosulphite, thiourea dioxide and sulphoxilic acid derivatives as reducing agents
- Caustic soda (sodium hydroxide)
- Sodium sulphate
- Polyacrylates and alginates as anti-migration agents in padding processes
- Formaldehyde condensation products with naphthalene sulphonic acid and lignin sulphonates as dispersing agents
- Surfactants (including ethoxylated fatty amines) and other components such as betains, polyalkylenamines

- Polyvinylpyrrolidone as levelling agent
- Hydrogen peroxide, sodium perborate, 3-nitrobenzenesulphonic acid as oxidants
- Soap.

Vat dyes are water insoluble after oxidation and therefore they can be largely eliminated by adsorption on the activated sludge in waste water treatment plants. Vat dyes contain heavy metal impurities (Cu, Fe, Pb, Ba, Mn) used during production. In some cases it is still difficult to keep these limits below the ETAD standards.

### 16.2.11 Pigments

The use of pigments in dyeing is limited, although they are widely used in printing. Pigments are insoluble in water and organic solvents. Due to lack of affinity to fibres the use of polymerising binder is essential for fixation. Pigments are mainly used for printing of cellulosic fibres and their blends with polyester.

### 16.2.12 Natural dyes

Before the discovery of the first synthetic dye in 1856, all the colourants used for the colouration of textiles were of natural origin, mainly plant sources, and a few derived from animal/insect sources. Structurally, there are large variations. After the discovery of synthetic dyes, their use diminished in industrial scale dyeing, but there is now a revival of natural dyes mainly due to environmental considerations. The majority of natural dyes require a metal salt as a mordant for dye fixation on the fibre. These dyes are mainly suitable for cellulosic, wool and silk fibres.<sup>14</sup>

Dyes are also classified according to their end-use properties, most notably their fastness under a variety of end-use conditions, such as light, laundering, rubbing (crocking), dry cleaning, etc. These properties, as customers' requirements, are taken into account during dye selection. However, customers generally have little knowledge of the environmental consequences of their selections. For maximum pollution prevention, the dyer should encourage the customer to consider more environmentally friendly dyes. Often, a slight change in hue or brightness requirements allows selection of different dyes and colourants that could potentially eliminate significant environmental problems (e.g. metals in waste water).

## 16.3 Environmental issues in dyeing

Commercial dyes are never 100% pure. Additional substances such as traces of unreacted dye intermediates and catalysts (if used), dispersing agents, diluents, etc., are always present to different extents. In addition to dyes any

dyeing operation will require chemicals/auxiliaries to facilitate the aqueous dyeing under suitable dyeing conditions to meet the commercial requirements. In the present section the effect of dyes and dyeing auxiliaries on the environment are highlighted in terms of human toxicity and environmental toxicity of dyes and dyeing auxiliaries.

### 16.3.1 Toxicity to humans

It is known that dye intermediates, dyes and even dyed fabrics can cause a wide variety of health problems ranging from skin rashes, headaches, lack of concentration, nausea, diarrhoea, fatigue, muscle and joint pain, dizziness, difficulty in breathing, irregular heartbeat and seizures. Symptoms in children include red cheeks and ears, dark circles under the eyes, hyperactivity, and behaviour or learning problems. In extreme cases some dyes also show health hazards leading to cancer.<sup>15</sup>

Human toxicity of textile dyes can be considered in terms of acute toxicity and chronic or genotoxicity.<sup>16</sup>

#### *Acute toxicity of textile dyes*

Acute toxicity involves oral ingestion and inhalation. The main problems of acute toxicity with textile dyes are skin irritation and skin sensitisation, caused mainly by reactive dyes for cotton and viscose, a few acid dyes on polyamide fibres and disperse dyes for polyester, polyamide and acetate rayon.<sup>17–23</sup>

#### *Reactive dyes*

Reactive dyes can cause problems for workers involved in the manufacture of the dyes and textile workers who handle the dyes in the dyeing process. There is evidence that some reactive dyes cause contact dermatitis, allergic conjunctivitis, rhinitis, occupational asthma or other allergic reactions in such workers. The problem is caused by the ability of reactive dyes to combine with human serum albumin (HSA) to give a dye–HSA conjugate, which acts as an antigen.<sup>3,24,25</sup>

A list of reactive dyes that have caused respiratory or skin sensitisation in workers on occupational exposure has been compiled by ETAD (Table 16.2).<sup>26</sup>

In order to minimise the risk from these dyes exposure to dye dust should be avoided. This may be achieved by using liquid dyes, low dusting formulations and by using the appropriate personal protective equipment.

After dyeing and fixation, reactive dyes have completely different toxicological properties because the reactive group is no longer present and the high wash fastness of the dyed fabric ensures that no dye is exposed to the skin of the wearer. Consequently, no cases of allergic reactions have been reported by consumers wearing textiles dyed with reactive dyes.<sup>3</sup>

Table 16.2 List of reactive dyes to be classified as respiratory sensitisers<sup>26</sup>

C.I. name	C.I. No.	CAS No.
Reactive Yellow 25		[72139-14-1](3Na)
Reactive Yellow 39	18971	[70247-70-0](2Na)
Reactive Yellow 175		[111850-27-2](2Na)
Reactive Orange 4	18260	[70616-90-9](3Na)
Reactive Orange 12	13248	[70161-14-7](3Na)
		[93658-87-8](xNa)
Reactive Orange 14		[12225-86-84](acid)
Reactive Orange 16		[20262-58-2](2Na)
		[106027-83-2](2Li)
Reactive Orange 64		[83763-57-9](xNa)
Reactive Orange 67		[83763-54-6](xNa)
Reactive Orange 86		[57359-00-9](3Na)
Reactive Orange 91		[63817-39-0](3Na)
Reactive Red 29		[94006-25-4](5Na)
		[70865-39-3](4Na)
Reactive Red 65		[70210-40-1](2Na)
Reactive Red 66	17555	[70210-39-8](2Na)
Reactive Red 123		[85391-83-9](xNa)
		[68956-17-1](2Na)
Reactive Red 219		[149057-72-7](4Na)
Reactive Red 225		[83399-95-5](xNa)
Reactive Violet 33		[69121-25-1](3Na)
Reactive Blue 114		[72139-17-4](2Na)
Reactive Blue 205		[85153-92-0](6Na)
Reactive Black 5	20505	[17095-24-8](4Na)

Source: Adapted from H Motschi, ETAD guidance on labelling of reactive dyes, *JSDC*, 116, (2000), 251.

### Disperse dyes

Certain disperse dyes have been implicated in causing allergic reactions, particularly when they are used for skin-tight, close-fitting clothes made from synthetic fibres. The perspiration fastness property of the dyes is important for whether an allergic response is caused or not. Polyester dyed with disperse dyes does not in general pose a problem since the perspiration fastness is high. However, problems can arise with polyamide or acetate rayon dyed with disperse dyes since the low perspiration fastness allows the dyes to migrate to the skin. Indeed, in the 1980s, some severe cases of allergic reactions were reported relating to stockings made of polyamide and, in the 1990s, to leggings made of acetate rayon.<sup>27-29</sup>

Since the report of these allergic reactions, the German Federal Institute for Consumer Protection and Veterinary Medicine evaluated the available literature and concluded that the disperse dyes listed in Table 16.3 represent a health risk to consumers and should not be used for dyeing.<sup>30</sup>

Table 16.3 Sensitising disperse dyes<sup>30</sup>

Dye	C.I. number	Hazard	R43	Dye type
Disperse Blue 1	64500			Aq
Disperse Blue 3	61505	Xi	X	Aq
Disperse Blue 7	62500			Aq
Disperse Blue 35	–	Xi	X	Aq
Disperse Blue 106	–	Xi	X	Aq
Disperse Blue 124	–	Xi	X	Azo
Disperse Orange 1	11080	Xi	X	Azo
Disperse Orange 3	11005	Xi	X	Azo
Disperse Orange 37	–	Xi	X	Azo
Disperse Red 1	11110	Xi	X	Azo
Disperse Red 15	60710			Aq
Disperse Red 17	11210			Azo
Disperse Yellow 1	10345			Nitro
Disperse Yellow 3	11855	Xn	X	Azo
Disperse Yellow 9	10375			Nitro
Disperse Yellow 39	–			Methine
Disperse Yellow 49	–			Methine

R43: May cause sensitisation by skin contact; Xi: Harmful to health/Irritating; X: Yes (applicable); Xn: not applicable Aq: Anthraquinone dye.

Source: Adapted from Swedish National Chemical Inspectorate, Chemicals in Textiles Report of a Government Commission 5/97.

Currently, there is no legal prohibition on these dyes in any country but some organisations, such as the International Association for Research and Testing in the Field of Textile Ecology, which bestows eco-labels on environmentally and toxicologically proven textiles, refuses eco-labels for some dyes.<sup>31</sup>

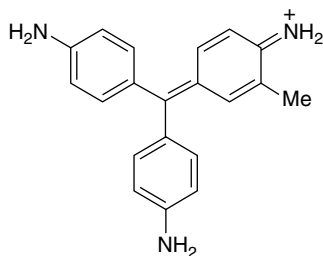
### 16.3.2 Chronic or genotoxicity of different dye intermediates and dye classes

Genotoxicity is the major long-term potential health hazard of certain textile dyes. This became apparent when a high incidence of bladder cancer was observed in plant workers involved in the manufacture of particular dyes during the period 1930–1960. The specific compounds involved (shown in Fig. 16.1) were fuchsine, auramine, benzidine and 2-naphthylamine.

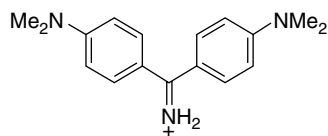
Strict regulations concerning the handling of all known carcinogens have been imposed in most industrial countries, which have caused virtually all dye companies to cease production of these compounds.<sup>3</sup>

#### *Effect of physical properties on genotoxicity*

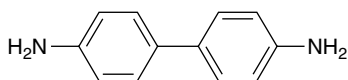
Before discussing the genotoxicity of different dye intermediates and dye classes it will be beneficial to understand the mechanism of genotoxic effect and the effect of the physical properties of genotoxic chemicals. Genotoxic



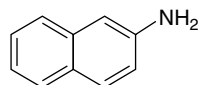
Fuchsine (C.I. Basic Violet 14)



Auromine (C.I. Basic Yellow 2)



Benzidine



2-Naphthylamine

16.1 Structures of fuchsine, auromine, benzidine and 2-naphthylamine.

chemicals such as mutagens and carcinogens damage DNA (deoxyribonucleic acid), the genetic blueprint material, usually by chemical reaction. Therefore, it follows that any genotoxic chemical must satisfy two criteria:

1. It must reach the DNA (which resides in the nucleus of the cell) in order to interact with the DNA.
2. It must possess the ability to interact with the DNA, usually by a chemical reaction.

In order to express a genotoxic effect, a chemical must first come into contact with the DNA present in a cell nucleus. To do this it must be able to transport across the protective cell membranes. Physical factors such as solubility and molecular size are of paramount importance in determining whether this transport occurs. In general, smaller molecules are transported across cell membranes more readily than larger molecules. Above a certain molecular size (MW > 800), molecules become too large to transport across cell membranes. Thus, molecular size offers one way of obtaining non-genotoxic chemicals. Indeed, this approach was adopted to produce non-toxic food dyes.

In the textile dye area, phthalocyanine dyes are probably too large to pass through the cell membranes and should be classed as non-genotoxic.

The two extreme cases of high water solubility on the one hand and total insolubility on the other hand generally result in non-genotoxic chemicals. Pigments, by definition, are insoluble in both water and organic solvents. This insolubility, combined with the relatively large size (0.1–3  $\mu\text{m}$ ) of pigment particles, which are aggregates of millions of individual molecules, ensures that most pigments are not transported across cell membranes. Consequently, the majority of pigments are non-carcinogenic. Molecules with high water

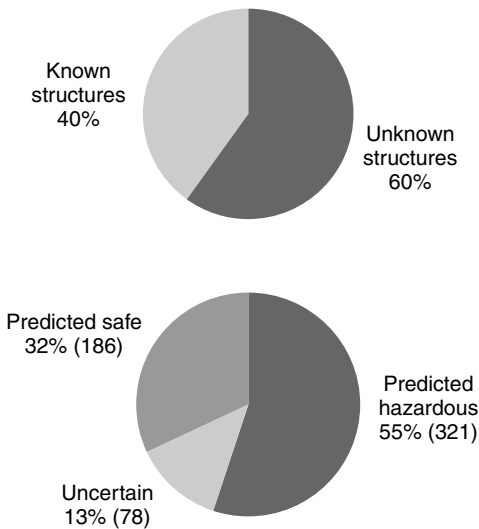
solubility are also non-genotoxic. There are two major reasons for this. First, the hydrophobic (fatty) nature of the cell membrane is impervious to the hydrophilic water-soluble molecules. Secondly, water-soluble molecules are generally excreted rapidly by a living organism. The best chemical grouping for imparting water solubility is the sulphonic acid ( $-\text{SO}_3\text{H}$ ) group. Carboxylic acid ( $-\text{COOH}$ ) groups and hydroxyl ( $-\text{OH}$ ) groups are also useful water-solubilising groups, especially when ionised. These three types of groups are employed extensively in textile dyes. A quaternary nitrogen atom ( $-\text{N}^+\text{R}_4$ ) also imparts water solubility. This group is found in cationic (basic) dyes.<sup>32-37</sup>

#### *Genotoxicity of dye intermediates*

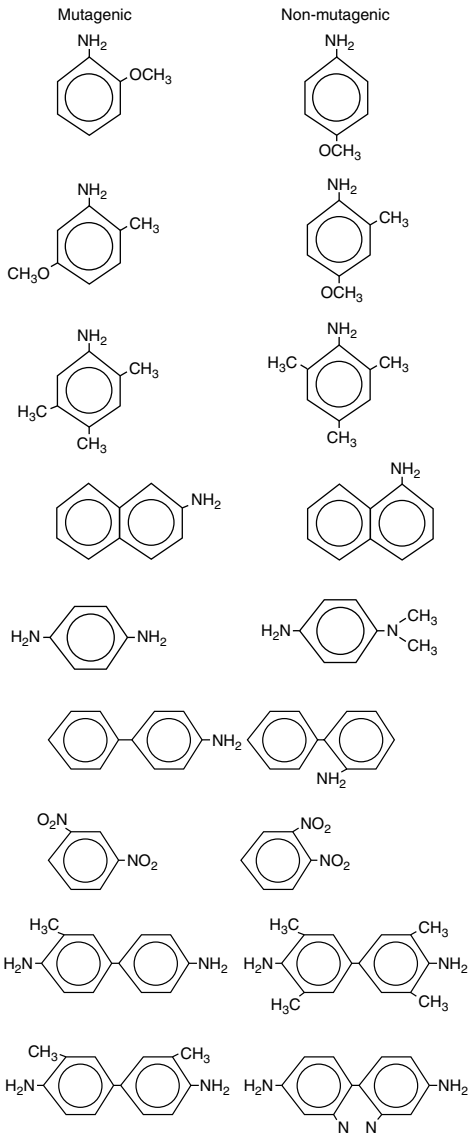
Close study of the dyes has revealed that carcinogenicity is linked to specific types of dye intermediates or metabolites, such as benzidines. Whaley<sup>38</sup> examined many dyes for evidence of a hazardous nature, based on their molecular structure. Of the 1460 dyes examined, the structures were found or known for 585 dyes, or approximately 40% of the total. Based on an assessment of likely formation of degradation products on reduction, 55% of these known dyes were predicted to be hazardous, and 13% were predicted to be uncertain in terms of safety (Fig. 16.2).

Since 1984, a concerted research effort has been made to develop dyes based on safer intermediates. Some safer intermediates, along with the older, traditional mutagenic intermediates, are shown in Fig. 16.3.

The old intermediates were adopted many years ago before development of the numerous tests now available to determine environmental effects.



16.2 Predicted hazardous nature of dyes.<sup>38</sup>



16.3 Some mutagenic dye intermediates and non-mutagenic alternatives.<sup>38</sup>



Responsible dye manufacturers have eliminated offending colours from their product lines; however, the widespread use of apparently harmful dyes indicates the need for the dyer to be vigilant when selecting dyes and to use care in handling all dyes. Responsible manufacturers now consider the environmental impact of the dyes they produce, in addition to their traditional considerations of economy, high wet fastness and high tinctorial value.<sup>39</sup>

### *Genotoxicity of different dye classes*

Azo dyes are by far the most important class of dye, accounting for over 50% of world annual production. Not surprisingly, toxicity of azo dyes has been studied extensively. As early as 1895 increased rates in bladder cancer were observed in workers involved in dye manufacturing. Since that time, many studies have been conducted showing the toxic potential of azo dyes. A broader understanding of the problem can be found in the works of Brown and DeVito<sup>40</sup> as well as Levine.<sup>41</sup> The carcinogen may be the dye itself, or it may be a metabolite of the dye. For water-insoluble, but solvent-soluble dyes, such as solvent dyes and disperse dyes, the dye is normally the carcinogen. For water-soluble dyes, it is a metabolite of the dye which is the carcinogen. Water-soluble azo dyes based on H-acid, J-acid and Gamma-acid represent a very important class of dyes for dyeing hydrophilic textiles such as cotton and viscose rayon. Cotton is the world's most widely used textile fabric so the tonnages of these water-soluble dyes are extremely large. The dyes are conveniently divided into two types:

1. Those which are capable of generating a carcinogenic metabolite.
2. Those that are not.

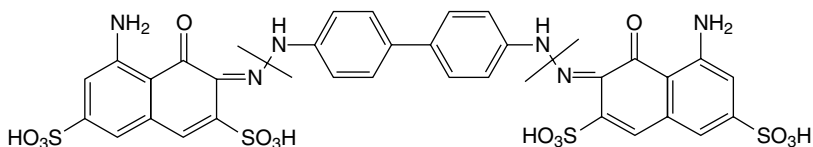
The workers who developed bladder cancer from handling dyes based on benzidine or 2-naphthylamine got the disease not from the dyes themselves, but from the benzidine and 2-naphthylamine metabolites.<sup>40-44</sup>

Figure 16.4 shows a typical water-soluble dye that can generate carcinogenic benzidine metabolite upon reduction in the animal body.<sup>34</sup>

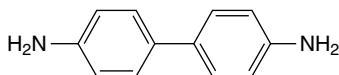
There are two main methods to circumvent the carcinogenicity of such dyes. The first is to use non-carcinogenic analogues of the amines in question, such as benzidine or its derivatives. For example, in Fig. 16.5, C.I. Direct Black 171 uses a non-carcinogenic aromatic benimidazol diamine instead of benzidine.<sup>33</sup>

Freeman and Rinde observed that when the C.I. Direct Black 38 based on benzidine was fed to Rhesus monkeys, benzidine was detected in their urine.<sup>37,45</sup>

The second way to avoid carcinogenicity is to ensure that all possible metabolites of the dye are water soluble. An excellent example of this principle is shown in Fig. 16.6, where the degradation of C.I. Food Black 2, a dye

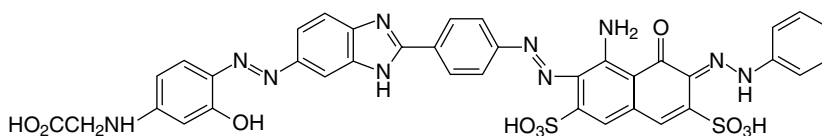


Water soluble Direct Dye

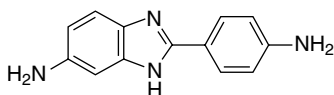


Benzidine

16.4 Typical water-soluble azo dye that generates carcinogenic benzidine.<sup>16</sup>



C.I. Direct Black 171

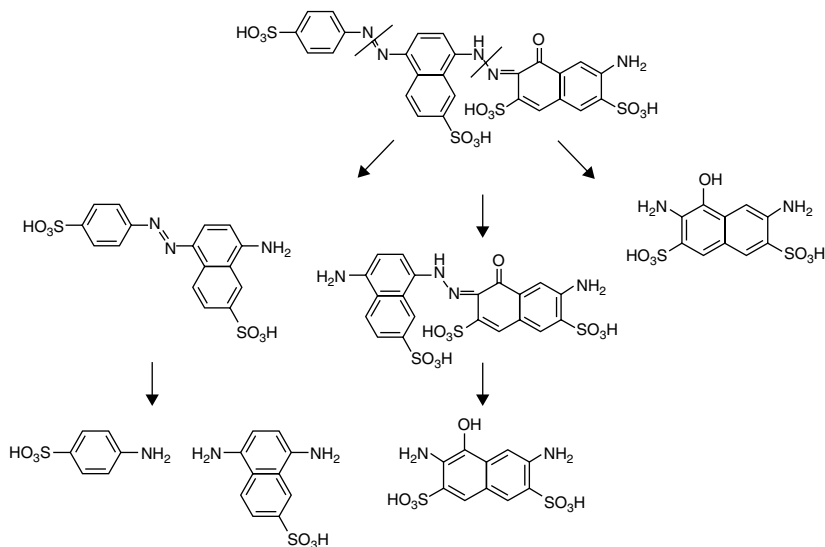


Benzimidazole diamine

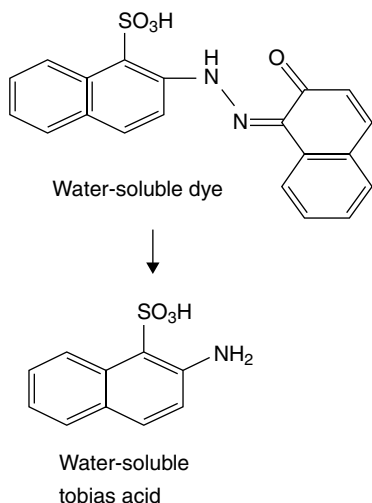
16.5 Typical water-soluble dye that generates non-carcinogenic aromatic benzimidazole diamine.<sup>16</sup>

used in black inks for ink-jet printers, gives metabolites of the dye which contain at least one water-solubilising sulphonyl group. This ensures that the dye itself, plus any of its metabolites, are water-soluble.<sup>33</sup>

Further examples of water-soluble dyes that generate water-soluble metabolites and are non-carcinogenic are given by Gregory.<sup>34</sup> The power of the water-solubilising sulphonyl group to detoxify dyes and intermediates is beautifully demonstrated by the dye in Fig. 16.7. This dye is non-carcinogenic. Upon reductive cleavage, it would produce, as one metabolite, 2-naphthylamine-1-sulphonyl acid (Tobias acid). As seen earlier, 2-naphthylamine is a potent human bladder carcinogen. However, the presence of just one sulphonyl group renders it harmless. Indeed, the



16.6 Probable degradation products of C.I. Food Black 2.<sup>16</sup>



16.7 Use of a water-solubilising sulphonic acid group in reductive cleavage of dyes to give a non-carcinogenic metabolite.<sup>16</sup>

sulphonic acid group is an excellent detoxifying group both for dyes and their intermediates.<sup>34</sup>

The position of a genotoxic group within a dye also determines whether or not the dye expresses genotoxicity. Care has to be exercised when using

isomers of carcinogens. Thus, 1-naphthylamine is non-carcinogenic. However, during its synthesis, some of the isomeric 2-naphthylamine, a known carcinogen, is produced. This carcinogenic impurity must be removed to a level below which it is not a problem. For dyes that use 1-naphthylamine, every batch must be checked to ensure that the level of 2-naphthylamine is below the recommended level.<sup>16</sup>

In Germany, bladder cancer is recognised as an occupational disease for textile workers.<sup>46</sup> Some dyes have the potential to release an aromatic amine that is known to be a rodent carcinogen upon metabolism in an organism and this has prompted some authorities to conclude that such dyes should be considered to be carcinogenic.<sup>47</sup>

This knowledge is the reason for the recommendation of the German MAK Kommission to handle the dyes in the same way as the amines which can be released under reducing conditions. Subsequently, the German, Dutch and Austrian authorities prohibited the use of such dyes in some consumer articles. Such dyes may not be used for textile, leather or other articles which have the potential for coming into direct and prolonged contact with human skin, e.g. clothing, bedding, bracelets, baby napkins, towels, wigs, etc. The ban, which applies across the EU, also covers the import and marketing of the above-mentioned articles dyed with these dyes. Table 16.4 lists the amines that are classified as carcinogenic and formed through cleavage of azo bonds of the azo dyes.<sup>48</sup>

ETAD has compiled a list of azo dyes which, upon reduction of the azo group, would form the aromatic amines shown in Table 16.4. The list includes more than 500 azo dyes, of which at least 142 are still available on the world market.

It has been suggested that when the fabric dyed with dyes which release carcinogenic amines (Table 16.4) comes into close contact with the human body the amines are leached out from the fabric due to human perspiration (these dyes usually have low perspiration fastness). The leached out dye is transferred into the body through skin pores. After intake into the human body these azo compounds may be cleaved by means of reduction during metabolism and then form the corresponding aromatic amines from which they had been synthesised. Intestinal bacteria are capable of azo cleavage; the liver also produces corresponding reductive enzymes. Furthermore, there are indications from experiments that azo cleavage may also take place during skin passage and that skin bacteria are capable of cleaving azo dyes.

Other suggested mechanisms for azo cleavage are as follows:

- Azo dyes with structures containing free aromatic amine groups that can be metabolically oxidised without azo reduction may cause toxicity.

Table 16.4 Carcinogenic aromatic amines defined by German MAK Kommission<sup>48</sup>

S no.	C.I. name	Category of carcinogen*
1	4-Aminobiphenyl	1
2	Benzidine	1
3	4-Chloro-o-toluidine	1
4	2-Naphthylamine	1
5	4-Aminoazobenzene	2
6	o-Aminoazotoluene	2
7	6-Methoxy-m-toluidine	-
8	o-Anisidine	2
9	p-Chloroaniline	2
10	5-Nitro-o-toluidine	3
11	4,4'-Diaminodiphenylmethane	2
12	3,3'-Dichlorobenzidine	2
13	3,3'-Dimethoxybenzidine	2
14	3,3' Dimethylbenzidine	2
15	4,4'-Methylenedi-o-toluidine	2
16	3,3'-Dichlorobenzidine	2
17	4,4'-Methylene-bis-[2-chloroaniline]	2
18	4,4'-Oxydianiline	2
19	4,4'-Thiodianiline	2
20	o-Toluidine	2
21	4-Methyl-m-phenylenediamine	2
22	2,4,5-Trimethylaniline	2

\*Category 1: Proven human carcinogen; 2: Proven animal carcinogen; 3: Suspected animal carcinogen.

Source: Adapted from ETAD Information No. 6, 'German ban of use of certain azo compounds in some consumer goods, revised version', Basle, (1998).

- Azo dye toxic activation may occur following direct oxidation of the azo linkage producing highly reactive electrophilic diazonium salts.<sup>40</sup>

Pigments containing the azo group which can degrade to carcinogenic aryl amines are virtually insoluble and are judged possibly not to be bio-available. In view of the fact that the new studies involving animal tests have shown that resorption of azo pigments can take place through the intestinal wall as well as uptake via inhalation, some risk cannot be ruled out. Other sources report that certain pigments contain toxic amines as impurities.

A ban applying to specific azo dyes in textiles, leather goods and similar consumer products entered into force in Germany, Netherlands and France in 1996. Subsequently it was adopted within the framework of EC Restriction Directive for harmonised rules on azo dyes in consumer goods. In 1998 the German ban also included pigments containing the azo group that can degrade to carcinogenic arylamines. German scientists claim that

pigments often contain residues/impurities of dyes with soluble arylamines. The German ban also established test methods. The test results must be confirmed by two of the four test methods specified. Forbidden arylamine may not be present in higher concentration than 30 mg/kg (30 ppm).

The risk represented by the dyes has also received attention in dye producing countries, such as Hong Kong, China, India and Turkey. In 1996 the Indian government proposed a ban on the manufacture, sale and use of 74 azo dyes found to be carcinogenic. The ban was partly a consequence of similar bans in Europe. The Indian government claimed that the ban will also protect domestic consumers from exposure to hazardous dyes. The use of 42 benzidine dyes in textile and leather has been prohibited in India since 1 February 1993.<sup>49</sup>

The ban on suspected azo dyes also exists in the USA and Canada. The eco-labels of various countries have also regulated the use of identified azo dyes. As a result of these efforts most of the dyestuff manufacturing countries voluntarily suspended the manufacture of suspected azo dyes and the problem of the use of these dyes is currently supposed to be non-existent.

Anthraquinone dyes have declined in importance, primarily because they have low-cost effectiveness due to low colour strength and relatively expensive manufacturing cost. Consequently, they have been studied less extensively than azo dyes. However, structure–activity relationships in anthraquinone dyes appear to follow a similar trend to those in azo dyes.<sup>50</sup>

Thus, anthraquinone dyes of the solvent or disperse class containing one or more primary amino or methylamino groups tend to be mutagenic or carcinogenic.<sup>3,33</sup>

Some cationic dyes, along with benzidine and 2-naphthylamine, were implicated in the high incidence of bladder cancer in the textile industry between 1930 and 1960. As seen earlier, the cationic (basic) dyes involved were fuchsine and auramine. Further cationic dyes have been found to be carcinogenic, such as the triphenylmethane dyes C.I. Acid Violet 49 and C.I. Basic Red 9, and several fluorescent red dyes, such as Pyronine B, are mutagenic.<sup>51</sup>

While the toxicological properties of synthetic dyes are very well tested scientifically and safety data sheets are available for each dye, similar study to that of azo dyes for natural dyes is not available. Many of the natural dyes are quite safe but a few are toxic. The example of logwood is given for illustration.

Logwood is a natural dye, capable of producing a range of colours such as violets, blue-greys and the best natural black, depending on the mordant used. However, the active ingredients, hematein and hematoxylin, are toxic when inhaled, absorbed through the skin or ingested. Care should be taken with this natural dye as with any of the harmful synthetic dyes.

Most natural dyes are not particularly toxic in themselves, but a mordant is invariably required for development of shade and dye fixation. Typically, a mordant is a heavy metal salt of aluminium, iron, copper, chromium or tin. Alum and ferrous sulphate are relatively safe mordants compared to copper and chromium. However, still they have to be used carefully. The fatal dose of alum is 30 g for an adult; the fatal dose for a child is, of course, far less, depending on body weight, perhaps as little as 3 g. Iron is toxic in overdose according to the United States Food and Drug Administration (FDA), but it will not harm the environment when disposed of. Tin and copper mordants have to be used with care. Chrome mordant is toxic and has both human and environment toxicity and is a known human carcinogen. Many eco-labels have fixed the optimum limits for these mordants to be released in the environment, particularly copper, tin and chromium.

### 16.3.3 Environmental toxicity of dyes and dyeing auxiliaries<sup>52</sup>

Environmental pollution due to dyeing is mainly related to water pollution. Due to the low vapour pressure of the substances in the dyebath, emissions to air are generally not significant. A few exceptions are thermosol dyeing, pigment dyeing and those dyeing processes where carriers are employed.

Water-polluting substances may originate from:

- the dyes themselves
- auxiliaries contained in the dye formulation
- basic chemicals (e.g. alkali, salts, reducing and oxidising agents)
- auxiliaries used in dyeing processes
- contaminants present on the fibre when it enters the process sequence (e.g. residues of pesticides on wool, cotton and spin finishes on synthetic fibres).

#### *Dyes*

Spent dyebaths after exhaust dyeing, residual dye liquors in pad dyeing and water from washing operations always contain a percentage of unfixed dye. The rates of fixation vary considerably among the different classes of dyes and may be especially low for reactive dyes in the case of cotton. Moreover, large variations are found even within a given class of colourants. As a consequence of incomplete fixation a percentage of the dyestuff used in the process ends up in the waste water.

In the aquatic environment, dyes can undergo bio-concentration, ionisation, abiotic oxidation, abiotic and microbial reduction, precipitation and ligand exchange. The ionic dyes such as acid, direct, basic and metal-complex

Table 16.5 Toxicity grading of dyes<sup>53</sup>

LD <sub>50</sub> (mg/kg)	Classification	No. of dyes	(%) Dyes
<25	Very poisonous		
25–200	Poisonous	44	1
200–2000	Harmful	314	7
>2000	Not classified	4103	92
Total		4461	100

*Source:* Adapted from Barclay S and Buckley C, Waste minimization guide for the textile industry: A step towards cleaner production, Appendix 3.10, *Dyes Environ*, January 2000; Desai C, Ecological and toxicological properties of dyes, *Colourage*, **39**(12), (1992), 51–54.

dyes will not volatilise whereas, in principle, solvent, disperse, vat and sulphur dyes have the potential to be volatile. Sorption should also play a major role as dyeing is a sorption process. Hydrolytic reactions are not important because if the dye survives the rigours of biological treatment processes, it is unlikely to degrade rapidly in the environment. Photochemical reactions may be important as dyes are good absorbers of solar energy. However, little information is available on this. It is expected that anionic dyes would react with ions such as calcium and magnesium to form insoluble salts and thereby reduce the concentration available for other biological reactions. Redox reactions should also be considered, as in early vat dyeing processes the dyes were reduced microbially before chemical replacements were introduced. Reduction in the environment would most likely occur under anaerobic conditions.<sup>53</sup>

Dyes give rise to public concern when even small concentrations (1 mg/L) are visible in the environment. Toxicity is determined by carrying out tests on animals (usually rats) to ascertain the single oral dose of dye that will kill 50% of the population in 14 days. This is known as the lethal dose (50) or LD<sub>50</sub> and the results are expressed in mg/kg of body weight. On the basis of these tests, toxicity grading can be made (Table. 16.5).

Aquatic toxicity is also expressed as LC<sub>50</sub> (measured in mg/L), which gives the concentration of a chemical that causes 50% of an experimental population of fish to die during 48 h. Table 16.6 gives the results of a study carried out by ETAD on 3000 commonly used dyes.<sup>54</sup>

It is difficult to assess the aquatic toxicity in terms of structure as a simple change in the position of substituents can alter the toxicity. The American Dye Manufacturers Institute (ADMI) carried out a survey in 1971 on the aquatic toxicity of 46 dyes tested on fish. The results given in Table 16.7 showed that cationic (basic) dyes were the most toxic due to their cationic nature, whereas direct and vat dyes were found to be non-hazardous.<sup>55</sup>



Table 16.6 Fish toxicity levels of common dyes<sup>53</sup>

LC <sub>50</sub> (mg/L)	% of dyes
<1	2
1–10	1
10–100	27
100–500	31
>500	28

Source: Adapted from Barclay S and Buckley C, Waste minimization guide for the textile industry: A step towards cleaner production, Appendix 3.10, *Dyes Environ*, January 2000, Desai C, Ecological and toxicological properties of dyes, *Colourage*, 39(12), (1992), 51–54.

Table 16.7 Aquatic toxicity of various dye classes<sup>55</sup>

Dye class	Number tested	Number toxic	% found to be toxic
Disperse	6	2	33.3
Acid	12	8	66.7
Mordant	1	1	100.0
Direct	14	1	7.1
Basic	5	5	100.0
Brightener	1	0	0.0
Sulphur	1	0	0.0
Vat	6	0	0.0
Fibre reactive	0	0	–

Source: Adapted from EPA, USA, 1996; Little L W and Lamb J C, Acute toxicity of 46 selected dyes to the fathead minnow *Pimephales promelas*, *American Dye Manufacturing Institute* (September, 1972).

At the time of the ADMI study, fibre reactive dyes that are now popular were not in widespread use. These would exhibit similar toxicity to acid and direct dyes except that they are typically accompanied in waste water in larger quantity because of low exhaustion and also the large amount of salt used during dyeing.

Brown and Anliker summarised the effects of textile effluent on the environment and the toxicity with respect to fish and other aquatic organisms, sewage bacteria and plants. They concluded that due to the vast number of different dyestuffs and processes in which they can be applied, an accurate environmental risk assessment can only be made on individual dyestuffs and in individual dye-houses.<sup>56</sup>

Dyes are stable against breakdown by many micro-organisms and most dyes do not biodegrade under aerobic biological treatments in a municipal sewage plant. Many dyes, including the azo dyes, degrade under anaerobic

conditions and the aromatic amines thus formed have been found to degrade further aerobically. Therefore, the aerobic conditions of rivers and lakes should degrade the amines formed from the biodegradation of azo dyes if they accumulate in the river sediments. Due to the recalcitrant nature of dyestuffs under aerobic processes, concern arose as to the toxicity of these compounds towards the micro-organisms. A screening method for determining the inhibitory effect of the dyestuffs on aerobic bacteria was developed by ETAD.<sup>57</sup>

Tests were performed on 202 dyestuffs and the results were reported as the 50% Inhibition Concentration ( $IC_{50}$ ) values. Dyes from the direct, disperse, reactive, vat, mordant, pigment, acid and solvent ranges gave  $IC_{50}$  values greater than 100 mg/L thus indicating that they had no toxic effect towards the micro-organisms at the concentration expected in textile effluents. However, dyes belonging to the cationic (basic) range gave  $IC_{50}$  values of less than 100 mg/L, which is in agreement with the results obtained by Ogawa *et al.* that basic dyes are inhibitory to micro-organisms.<sup>58</sup> From these tests, and the general experience of ETAD, it was concluded that although dyes may cause concern at sewage works due to their colour, there should be no concern as to their toxicity. The exception to this ruling is the benzidine-based dyes, the manufacture of which is prohibited by ETAD members.<sup>59</sup>

Some dyes are adsorbed 40–80% by the biomass. Of the 87 dyes studied, 62% had significant colour removal due to sorption. This is referred to as bio-elimination. With acid dyes, their high solubility causes low adsorption and this is based on the number of sulphonic acid groups. Reactive dyes also show little adsorption, but this, however, is not dependent on the sulphonated groups or ease of hydrolysis. Direct and basic dyes show high adsorption and disperse dyes show high to medium adsorption.<sup>53</sup>

Other key issues related to water pollution due to dyes are AOX emissions and presence of metal in the dye molecule.<sup>60</sup>

Dyestuffs containing organically bound halogens (except fluorine) are measured as AOX. Vat, disperse and reactive dyes are more likely to contain halogens in their molecular structure.

The content of organically bound halogen can be up to 12% on weight for some vat dyes. Vat dyes, however, usually show a very high degree of fixation. In addition, they are insoluble in water and the amount that reaches the effluent can be eliminated with high efficiency in the waste water treatment plant through absorption on the activated sludge.

In contrast, reactive dyes have low fixation (the lowest level of fixation is observed with phthalocyanine based reactive dyes) and their removal from waste water is difficult because of the low biodegradability and/or low level of adsorption of the dye onto activated sludge during treatment. The halogen in MCT (monochlorotriazine) reactive groups is converted into the harmless chloride during the dyeing process; it is therefore assumed that the

MCT reactive groups react completely by fixation or hydrolysis so that they do not contribute to AOX emissions. However, many commonly used poly-halogenated reactive dyes, such as DCT (dichlorotriazine), DFCP (difluoro-chloropyrimidine) and TCP (trichloropyrimidine) and bifunctional reactive dyes contain organically bound halogen even after fixation and hydrolysis. Bound halogen is also found in discharges of dye concentrates (pad dyeing, dye kitchen) and non-exhausted dyebaths that may still contain unreacted dyestuff.

For the other classes of colourants the AOX issue is not relevant because, with few exceptions, halogen content is usually below 0.1%. Strict limits are set by the EU eco-label and German legislation. Extensive investigation of AOX in textile effluents was performed, but AOX as an indicator remains a matter of discussion.

It should be noted that AOX from dyes do not have the same effect as the AOX derived from chlorine reactions (haloform reaction, in particular) arising from textile processes such as chlorine bleaching and wool shrink-resist treatments, etc. Dyestuffs are not biodegradable compounds and the halogens in their molecule should not give rise to the haloform reaction (the main cause of hazardous AOX).<sup>61</sup>

Metals can be present in dyes for two reasons. First, metals are used as catalysts during the manufacture of some dyes and can be present as impurities. Second, in some dyes the metal is chelated with the dye molecule, forming an integral structural element. Table 16.8 lists the metal content of some dyes.

The limits of discharge for heavy metals are stringent as they can be toxic to animals and aquatic life. Metal-complex dyes contain chelated chromium, cobalt, copper and nickel. Some cationic dyes contain zinc and trace

*Table 16.8* Heavy metal content of dyes<sup>62</sup>

Metal	Typical conc. ppm	Dye type with highest metal content
Arsenic	<1–1.4	Reactives
Cadmium	<1	All types
Chromium	3–83	Vat
Cobalt	<1–3.2	Acid
Copper	33–110	Vat
Lead	6–52	Reactives
Mercury	0.5–1	Vat
Zinc	3–32	Basic

*Source:* Adapted from EPA, USA, 1996; American Dye Manufacturers Institute (ADMI). Untitled presentation at American Association of Textile Colorists and Chemists (AATCC) Annual Technical Conference (28–30 September 1972).

concentrations of mercury, cadmium and arsenic can be present as impurities from intermediates.

Dye manufacturers are now putting more effort into reducing the amount of metals present as impurities. This can be done by selection of starting products, removal of heavy metal and using suitable solvent for the reaction in the absence of metal. ETAD has established limits for the content of heavy metal in dyestuffs. The values have been set to ensure that emission levels from a 2% dyeing and a total dilution of the dye of 1:2500 will meet the known waste water requirements.

Examples of dyes containing bound metals are copper and nickel in phthalocyanine groups, copper in blue copper-azo-complex reactive dyes and chromium in metal-complex dyes used for wool silk and polyamide. The total amount of metallised dye used is decreasing, but there are still domains where phthalocyanine dyes cannot be easily substituted, e.g. certain shades such as greens and turquoise blues. The presence of the metal in the metallised dyes can be regarded as a less relevant problem compared to the presence of free metal impurities, provided that high exhaustion and fixation levels are achieved and that measures are taken to minimise losses from handling, weighing, drum cleaning, etc. Moreover, since the metal is an integral part of the dye molecule, which is itself non-biodegradable, there is very little potential for it to become bio-available. It is also important to take into account that treatment methods such as filtration and adsorption on activated sludge, which remove the dye from the waste water, also reduce almost proportionally the amount of bound metal in the final effluent.<sup>62</sup>

#### *Auxiliaries contained in dye formulations*

Depending on the dye class and the application method employed (e.g. batch or continuous dyeing) different additives such as dispersants, salts, powder binding agents, anti-foaming agents, anti-freezing agents, thickeners, buffer systems, etc., are present in the dye formulations. Since these substances are not absorbed/fixated on the fibres, they are completely discharged in the waste water.

While these additives are not toxic to aquatic life, they are in general poorly biodegradable and not readily bio-eliminable. This applies in particular to the dispersants present in the formulations of vat, disperse and sulphur dyes. These dyes are water insoluble and need special auxiliaries in order to be applied to the textile in the form of aqueous dispersions. These dispersants consist mainly of naphthalene sulphonate-formaldehyde condensation products and lignin sulphonates, but sulphomethylation products derived from the condensation of phenols with formaldehyde and sodium sulphite can also be found. Other not readily eliminable additives are acrylate and CMC-based thickeners and anti-foam agents.

The difference between liquid and powder formulations should also be mentioned. Dyes supplied in liquid form contain only one third of the amount of dispersing agent normally contained in powder dyes. The reason for this difference stems from the manufacturing process of powder dyes: the very small particles generated during grinding must be protected during the subsequent drying process and this is possible only by adding high proportions of dispersing agents.<sup>60</sup>

#### *Basic chemicals and auxiliaries used in the dyeing process<sup>60</sup>*

Regarding the environmental concerns associated with the chemicals and auxiliaries used in dyeing processes it is worth mentioning a few key issues.

Waste water from sulphur dyeing contains sulphides used in the process as reducing agents. In some cases the sulphide is already contained in the dye formulation and in some other cases it is added to the dyebath before dyeing. In the end, however, the excess of sulphide ends up in the waste water. Sulphides are toxic to aquatic organisms and contribute to increasing chemical oxygen demand (COD) load. In addition, sulphide anions are converted into hydrogen sulphide under acidic conditions, thereby giving rise to problems of odour and corrosivity.

Sodium hydrosulphite (also called sodium dithionite) is another sulphur containing reducing agent, which is commonly used in vat dyeing, and also as reductive after-cleaning agent in polyester dyeing. During the dyeing process sodium hydrosulphite is converted into sulphite (toxic to fish and bacteria) and in some cases this is further oxidised into sulphate which may cause corrosion of concrete pipes or may be reduced under anaerobic conditions into hydrogen sulphide.

A second issue is that of oxidising agents. Dichromate should no longer be used in Europe as an oxidising agent when dyeing with vat and sulphur dyes, but it is still widely used for the fixation of chrome dyes in wool dyeing. Cr III exhibits low acute toxicity, while Cr VI is acutely toxic and has been shown to be carcinogenic towards animals. During the dyeing processes with chrome dyes, Cr VI is reduced to Cr III if the process is under control. Nevertheless, emissions of Cr VI may still occur due to inappropriate handling of dichromate during dye preparation (care must be taken as dichromate is carcinogenic and may cause health problems for workers handling it). Emissions of trivalent chromium in the waste water can be minimised but cannot be avoided, unless alternative dyestuffs are applied.

The use of bromate, iodate and chlorite as oxidising agents in vat and sulphur dyeing processes and the use of hypochlorite as stripping agent for decolouring faulty goods or for cleaning dyeing machines may produce AOX emissions. However, only hypochlorite and elemental-chlorine-containing compounds (e.g. certain chlorite products that contain Cl<sub>2</sub> or use of

**Table 16.9** Typical salt application for direct and reactive dyes on cotton<sup>63</sup>

Shade	Dye o.w.f. (%)	Amount of salt direct dyes (g/L)	Amount of salt reactive dyes (g/L)
Paste/light	<1.5	2.5–7.5	30–60
Medium	1.0–2.5	7.5–12.5	70–80
Dark	>2.5	12.5–20	80–100

*Source:* EPA, USA, 1996; Peters R H, *Textile Chemistry – The Physical Chemistry of Dyeing*, Vol. III, New York, Elsevier Scientific Publishing Company (1975).

chlorine as activator for formation of chlorine dioxide gas) are likely to give rise to hazardous AOX.

Another topic concerns the use of salts such as sodium chloride or sodium sulphate in dyeing processes to promote dye exhaustion or level dyeing. In particular, large amounts of salt are used in cotton batch dyeing processes with reactive dyes. The amount of salt employed is quite significant compared to other classes of dyestuffs, for example direct dyes, and efforts have been made by dye manufacturers to solve this problem (Table 16.9).

In addition to the use of salt as raw material, neutralisation of commonly used acids and alkalis produces salts as by-products.

Salts are not removed in conventional waste water treatment systems and they are therefore ultimately discharged in the receiving water. Although the mammalian and aquatic toxicity of the commonly employed salts is very low, in arid or semi-arid regions their large-scale use can produce concentrations above the toxic limit and increase the salinity of the groundwater. Countries have set emission limits at 2000 ppm or below. River quality standards must also be taken into account.<sup>63</sup>

A fourth issue is carriers. Carriers for polyester dyeing were widely employed in the past. However, their use has now been reduced due to ecological and health problems and also with the advent of pressurised dyeing vessels enabling the dyeing of polyester to be carried out at temperatures above the fibre T<sub>g</sub>. They are still an issue in dyeing of polyester in blend with wool. Carriers may already be added to the dyes by manufacturers. In this case textile finishers will have little knowledge of the loads discharged. Carriers include a wide group of organic compounds; many of them are steam volatile, poorly biodegradable and toxic to humans and aquatic life. However, they usually have high affinity for the fibre (hydrophobic types), 75–90% is absorbed by the fibre and only the emulsifiers and the hydrophilic-type carriers such as phenols and benzoate derivatives are found in the waste water. The carriers that remain on the fibre after dyeing and washing are partially volatilised during drying and fixing operations and can give rise to air emissions. Traces can still be found on the finished product, thus representing a potential problem for the consumer.

Other substances that may be encountered in the dyeing auxiliaries and that may give rise to water pollution are as follows:

- Fatty amine ethoxylates (levelling agent)
- Alkylphenol ethoxylates (APEO) (levelling agent)
- Quaternary ammonium compounds (retarders for cationic dyes)
- Polyvinylpyrrolidone (levelling agent for vat, sulphur and direct dyes)
- Cyanamide-ammonia salt condensation products (auxiliaries for fastness improvement)
- Acrylic acid-Maleic acid copolymers (dispersing agent).

Metal-complexing agents include:

- Ethylenediamine tetraacetate (EDTA)
- Diethylenetriaminepentaacetate (DTPA)
- Ethylenediaminetetra(i)thylenephosphonic acid (EDTMP)
- Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP).

All these auxiliaries are water-soluble, poorly biodegradable and can pass untransformed or only partially degraded through waste water treatment systems. In addition, some of them are toxic (e.g. quaternary amines) or can give rise to metabolites which may affect reproduction in the aquatic environment, e.g. APEO.

## **16.4 Environmentally friendly dyeing of cotton with reactive dyes**

Presently, most of the reactive dye manufacturers are addressing two major problems associated with the reactive dyes, namely, colour in the effluent and minimisation of salt usage.

### 16.4.1 Colour in the effluent

Removal of colour from the effluent is one of the expensive approaches to the end of pipe technology. Therefore, it is necessary to find suitable alternatives. In exhaust dyeing, the use of reactive dyes is a major source of concern. The vat, sulphur and azoic dyes exhibit a high degree of exhaustion and the insoluble unfixed dye can readily be removed as part of the primary flocculation process. Whereas in the case of reactive dyes, sometimes as high as 30% dye remains unbound during primary treatment and needs to be treated either on site as a secondary process after biological oxidation or at a municipal sewage works. The adsorption of hydrolysed reactive dye on biomass is not as efficient as of other water-soluble dye classes.

Unrelenting pressure to regulate industrial effluent discharge has led to the development of new reactive dyes, machinery and processes to minimise waste and colour in the effluent. The development of bifunctional reactive dyes is important from this point of view.

### 16.4.2 Bifunctional reactive dyes

Bifunctional reactive dyes consist of two reactive groups separated from each other which are capable of forming covalent bonds with the fibre. These bifunctional dyes can be of two types: (i) those consisting of two similar reactive groups (homo-bifunctional reactive dyes) and (ii) those with two different reactive groups (hetero-bifunctional reactive dyes). These dyes offer very high levels of fixation in exhaust dyeing. If one of the reactive groups hydrolyses during the dyeing process, the other one can still chemically react with the hydroxyl groups of cellulose.<sup>64</sup>

Examples of these high-fixation dye ranges are Cibacron FN, Cibacron H (Ciba), Drimarene HF (Clariant), Levafix CA (Dystar), Procion H-EXL/XL+ (Dystar) and Sumifix HF (Sumitomo).

In the case of mono-functional dyes, the fixation rate is approximately 60% so that 40% of the dye applied is lost in the effluent. In the case of bifunctional reactive dyes, 80% fixation rate is achieved. The immediate consequence is a significant reduction of unused dyestuff ending in the waste water stream. Two or even three reactive groups in a dye molecule do not guarantee 100% fixation efficiency and thus a thorough wash-off procedure is essential, particularly in heavy shades. Even if 99% fixation of reactive species occurs, there will still be a need for some form of wash-off to remove hydrolysed dye. Perhaps the answer may be the design of more effective after-treatment agents to interact with the hydrolysed dye to be chemically immobilised in the fibre.<sup>65</sup>

The tinctorial strength of new reactive dyes has improved significantly. This means that deeper and more intense shades are possible with less dye than necessary with other dyes or dye classes. Less dye is therefore left in the effluent, but the amount of visible colour may be still high.

Post-rinsing to obtain the required level of wet fastness can be performed quickly and with relatively little energy and water. Some new reactive dyes have molecules especially designed to show reduced affinity when they are in the hydrolysed form, which means that they have excellent wash-off properties.

A recent innovation from Dystar (Procion XL+ dyes) allows much shorter processing time by combining the pre-treatment and dyeing steps. Savings of up to 40% in water and energy consumption and more than 30% of salt are claimed.



High-fixation reactive dyes can be applied in all types of dyeing machines, but offer particular advantage for the most modern low liquor ratio dyeing machines. Thus additional advantages in terms of reduced energy and water consumption can be exploited. In particular, new reactive dyes with very good solubility can be applied at ultra-low liquor ratios.

Compared to conventional reactive dyes, bifunctional reactive dyestuffs are more expensive, but the higher fixation efficiency, the savings on salt usage and the reduced water and energy consumption lead to a significant reduction of total cost.

### 16.4.3 Dye liquor wastage

Minimisation of dye liquor wastage is a major environmental consideration in a continuous dyeing process to reduce colour in the effluent. At the end of every dyeing, there is liquor left in the pad trough as well as in the stock tank. Monforts and Ramische Kleinwefers companies have developed pad troughs with 10–15 L capacity.

### 16.4.4 Minimising usage of chemicals

Some of the approaches to minimise the use of chemicals are as follows:

- Dyeing at low liquor ratio
- Right-first-time approach
- Process innovations in continuous dyeing
- Use of low-salt reactive dyes.

### 16.4.5 Dyeing at low liquor ratio

The average consumption of water per kilogram of finished fabric is around 80–100 L. Lowering of liquor ratio reduces the volume of water used and the waste generated. Apart from the easier handling of lower volume of effluent, the dosing of chemicals and auxiliaries in the dyebath is done on the basis of g/L of liquor. This significantly reduces the quantities of chemicals and auxiliaries and finally the effluent load. In reactive and vat dyeing systems, a change of liquor ratio from 1:10 to 1:5 brings about a decrease in pollution load of about 40%. Low and ultra-low liquor dyeing machines are now available to achieve this goal.

### 16.4.6 Right-first-time approach

It is important to follow carefully the dyestuff manufacturer's recommendations for salt, alkali usage, temperature, time, etc., to ensure optimum

fixation levels and right-first-time production thereby avoiding the need to make shading additions. Computer colour matching should help in this regard.<sup>66,67</sup>

#### 16.4.7 Process innovations in continuous dyeing

Continuous dyeing of cotton with reactive dyes is carried out by cold pad-batch, pad-dry-thermofix, pad-steam and pad-dry-chemical pad-steam processes. These involve the use of various chemicals such as urea, soda ash, caustic soda, salt and sodium bicarbonate which cause loading of the effluent to various extents.

In the pad-dry-bake process, 200 g/L urea is used. Such a large quantity of urea decomposes during curing, producing an unpleasant odour. There is also an increase in nitrogen content of effluent, affecting biological treatment. The environmental impact of urea can be reduced by replacing part of the urea with dicyandiamide (e.g. by using 60 g/L urea and 15 g/L dicyandiamide) instead of 200 g/L urea in a pad-bake process to produce satisfactory dyeing.<sup>68</sup>

Zeneca in collaboration with Monforts has developed an interesting variant to reduce the chemical usage in continuous dyeing using highly reactive dichlorotriazinyl Procion MX dyes and sodium bicarbonate. The method (E Control) involves the fixation of dye under controlled relative humidity conditions of 25–30% in a hot flue dryer. The dyeing is carried out continuously using pad-dry-wash sequence. The fixation is as high as that in the pad-steam process.<sup>69</sup>

#### 16.4.8 Low-salt reactive dyes

Substantial quantities of electrolytes, such as sodium chloride and sodium sulphate, are used for the dyeing of cotton with reactive dyes. Exhaust dyeing with 10:1 liquor-to-material ratio needs a salt concentration of 30–80 g/L. This corresponds to 300–800 g salt per kg of dyed cotton. During effluent treatment, only a small quantity of salt is removed. Thus, a major quantity of salt enters the environment on discharge of effluent treated water. High salt concentration in effluent has the following disadvantages:

- Rivers and lakes get polluted with effluent containing high salt concentration.
- Fresh water organisms suffer toxic effects.
- In regions with scarce fresh water resources, such water has to be used for irrigation.
- If salt concentration is too high, soil may become overloaded with salt, making the land infertile and ultimately useless.

Ciba Speciality Chemicals has introduced low-salt Cibacron LS dyes which require only 20 g/L salt, whereas the conventional reactive dyes require 60–80 g/L salt for exhaustion. Thus reduced salt consumption has positive effects on effluent salinity and smooth running of waste water treatment plants. Low-salt reactive dyes are high affinity dyes, which makes them less easy to wash off than low to medium-affinity types. However, dyes with low affinity in the hydrolysed (unfixed) form are increasingly available, making post-rinsing operations much easier. To give the dyer the high flexibility needed, dye manufacturers have developed trichromatic combination dyes with high mutual compatibility (by matching the affinity and reactivity of each dye and minimising interactions among components). Products with very similar application properties are now available. Thus right-first-time production is claimed.

Low-salt reactive dyes were introduced first in areas having arid climate conditions and negative water balance (e.g. North Carolina in the USA and Tirupur, Tamil Nadu in India). They have also being successful in regions where dye-houses discharge directly to fresh water and there is a need to minimise salination effects.<sup>70–74</sup>

#### 16.4.9 Omitting the use of detergents in after-washing

Both international literature and practical experience in textile mills show that detergents do not improve removal of hydrolysed reactive dyestuffs from the fabric. Tests carried out with rinsing at 90–95°C have shown that rinsing is more effective and faster at high temperatures. About 30% more unfixed hydrolysed reactive dyestuff is rinsed out after 10 min of rinsing at 95°C than at 75°C.

Most often fastness of the dyed goods is better after the hot rinsing than after the traditional rinsing with detergents, complexing agents and neutralisation in the first rinse.

The main benefit of this approach is the reduction in consumption of detergents and pollution load discharged to the waste water. The average potential load reduction can be in the order of 1 kg detergent, 1 kg complexing agent and 1 kg acetic acid per 100 kg of textile.<sup>75–77</sup>

### 16.5 Alternative reducing systems for the dyeing of cotton with vat and sulphur dyes

#### 16.5.1 Vat dyes

Vat dyes are applied by using sodium hydrosulphite (sodium dithionate) as reducing agent and sodium hydroxide as an alkali. Some by-products of sodium hydrosulphite are acidic in nature, necessitating overdosing

of sodium hydroxide over stoichiometric requirement. A few of the by-products formed are sulphur compounds like  $\text{Na}_2\text{S}$  and  $\text{NaHS}$ , which pollute air through the formation of  $\text{H}_2\text{S}$ . At the same time, the salts of sulphur in the form of sulphate and sulphites ( $\text{Na}_2\text{SO}_3$ ,  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ ) contaminate sewage, lower its pH and show corrosive action on concrete pipes. Other problems associated with the use of sodium hydrosulphite are its cost and low storage stability.<sup>78</sup>

To overcome these problems, attempts were made by several researchers to develop alternative reducing systems which are eco-friendly in nature. Such new systems include electrochemical reduction, use of organic reducing agents like hydroxy acetone and iron (II) complexes. In the electrochemical reduction method, the dye is directly reduced by contact between dye and electrode, though a reducing agent must be added to the reduced dyebath to ensure corresponding stability of the reduced liquor. However, the dyestuff requirement to produce a specific shade is higher.<sup>79,80</sup>

Iron (II) salts have been widely used since ancient times to reduce vat dyes through a technique known as the *Copperas* method in which  $\text{FeSO}_4$  and  $\text{Ca(OH)}_2$  are used. The dyebath produced in this way resulted in bulky sediments due to poor solubility of  $\text{Fe(OH)}_2$ .<sup>81</sup> It has been found that  $\text{Fe(OH)}_2$ , produced via reaction of iron (II) salts with  $\text{NaOH}$ , can be complexed and taken into solution with the help of gluconic acid to obtain the desired reduction potential. The dye reduction and dyeing is carried out at  $60^\circ\text{C}$ . It is claimed that the system is environmentally friendly as during the neutralisation of the effluent, the free  $\text{Fe(OH)}_2$  is produced which gets converted to  $\text{Fe(OH)}_3$  and acts as flocculant. Thus, the problems associated with the use of sodium hydrosulphite as a reducing agent have been eliminated in this new technique.<sup>82</sup> This concept of the use of iron (II) complexes is further extended by Chavan and Chakraborty based on alkanol amines as single ligand system for dyeing of cotton with indigo, and double ligand system based on alkanol amine and organic acid for vat dyeing. It is reported that such iron (II) complexes not only totally replace sodium hydrosulphite, but also the vatting and dyeing can be carried out at room temperature.<sup>83–86</sup>

## 16.5.2 Sulphur dyes

Sodium sulphide is commonly used for the reduction in the application of sulphur dyes on cotton. Residual sodium sulphide acts as contaminant in the effluent. Sodium sulphide causes no marked odour nuisance above pH 9.0 but in acidic pH, gaseous  $\text{H}_2\text{S}$  is liberated, giving an unpleasant smell of rotten eggs which is toxic when inhaled. Its odour threshold value is 10 ppm.<sup>87</sup>

In order to overcome the environmental problems associated with sodium sulphide glucose can be thought of as an environmentally friendly substitute. Glucose has long been known as a reducing agent for sulphur dyes. Sulphur

Black and Indocarbon dyes were almost always reduced with glucose in the one-stage printing process. In exhaust dyeing, however, glucose at first gave unsatisfactory results, especially in open dyeing machines such as the jigger and winch. This was because the dye yield was highly dependent upon temperature. Only at constant temperature above 90°C were reasonable results obtained. Chavan and Vhanbatte obtained glucose by acid hydrolysis of molasses and cane sugar. On the basis of detailed investigations of various parameters, such as concentration of glucose, caustic soda, temperature and time, they concluded that at dyeing temperature of 90°C, glucose gives a colour yield equivalent to that obtained with sodium sulphide. The Century mill at Mumbai, India also established, on commercial scale, that sodium sulphide can be totally replaced with glucose obtained from hydrolysis of starch. Other sugars and related substances like hydroxy acetone have been examined but none of them was found to offer any advantage over glucose.<sup>88-92</sup>

Bechtold *et al.* have shown that it is possible to reduce Sulphur Black 1 by cathodic reduction. The process may be used for continuous dyeing without using conventional reducing agent such as sodium sulphide.<sup>93</sup>

## 16.6 Environmentally friendly dyeing of wool

### 16.6.1 Low-chrome and ultra-low-chrome after-chroming methods for wool

Chrome dyeing of wool is still important for deep shades at economical price with excellent fastness properties. The after-chrome method is the most widely adopted technique for the application of chrome dyes, and chromium (as sodium or potassium dichromate) is the metal used almost universally as mordant. In the application of chrome dyes, inefficient chroming methods can lead to the discharge of chromium in spent dye liquors. In order to minimise the amount of residual chromium in the final effluent much attention has been given to the low-chrome (stoichiometric) and ultra-low (sub-stoichiometric) chrome dyeing techniques, where only the minimum amount of dichromate required to form the dye complex in the fibre is dosed.

During the last 10–15 years, so-called low-chrome dyeing technology has been increasingly used. The method consists of stoichiometric dosage of chromium (up to a maximum of 1.5% o.w.f.) together with careful pH-control (3.5–3.8) and optional addition of a reducing agent, which assists in the conversion of Cr VI to Cr III and promotes its exhaustion onto the fibre.

Every major chrome dye manufacturer has published data relating to chrome additions and dyeing techniques that have been widely adopted (e.g. Bayer, Ciba-Geigy, Sandoz).

By the use of low-chrome techniques it is possible to reduce residual Cr III in the spent chroming bath from about 200 mg/L (typical of conventional

process) to about 5 mg/L in practical mill conditions. Residual Cr VI is almost eliminated.

Ultra-low chroming techniques are applied to achieve even lower residual chromium levels or in particular cases (e.g. wool that has to be dyed in deep shades) when low-chroming techniques cannot guarantee residual chromium levels below 5 mg/L in the spent chroming bath, chrome is dosed sub-stoichiometrically, based on the dye uptake of the fibre. In order to ensure accurate dosing and minimum handling of hazardous chemicals by the operator, the application of the low-chroming/ultra-low chroming techniques requires the use of automated dosing and dispensing system for dichromate, dyes and pH-control. The required amount of dichromate is fed directly to the dyeing machine through pipe work (no manual transfer, no human contact, no losses).<sup>94,95</sup>

## 16.6.2 Chromium-free dyeing of wool

Low-chrome dyeing techniques allow a considerable improvement in the efficiency of this process, but they cannot avoid the presence of free chromium in the water effluent and in the sludge. Furthermore, many eco-label initiatives discourage the use of chrome mordant dyes. The use of chrome dyes was considered unavoidable for certain types of wool articles, in particular for dark shades, due to the excellent wet fastness of these dyes. However, new reactive dyestuffs have been put on the market that can provide levels of fastness comparable with those achievable with chrome dyes, even for dark shades. These new colourants are bifunctional reactive dyestuffs generally containing bromo acrylamide or vinylsulphone reactive groups. The dye range is based on a trichromatic system, where Lanazol Yellow CE (or Golden Yellow CE), Red CE and Blue CE can be used for different shades and Lanazol Navy CE and Black CE for highly fast navies and blacks. Dyeing cycles are reported to be longer when dyeing with reactive dyes, due to rinsing and clearing. Fastness properties can be very good and even comparable/equivalent to those obtained with chrome dyes.

Thus by changing over to reactive dyestuffs, the handling of hexavalent chromium, which requires special safety precautions due to its chronic toxicity and carcinogenic effects, can be avoided.<sup>96</sup>

## 16.7 Environmentally friendly dyeing of polyester

### 16.7.1 Exhaust dyeing of polyester and polyester blends with carrier-free dyeing techniques or with the use of environmentally optimised carriers<sup>97</sup>

Exhaust dyeing of polyester is usually carried out at high temperature and pressure conditions 130°C using high temperature high pressure (HTHP)

dyeing machines. However, such dyeing conditions are harmful to blends like polyester/wool. Therefore in such cases it is essential to carry out dyeing at 95–100°C by using carriers. In dyeing and rinsing a significant amount of carrier is emitted to waste water. The fraction that remains on the fibre may be emitted to air during subsequent drying and heat setting.

Active substances used in carrier formulations include:

- chlorinated aromatic compounds (mono-chlorobenzene, trichlorobenzenes, etc.)
- o-phenylphenol
- biphenyl and other aromatic hydrocarbons (trimethyl benzene, 1-methyl naphthalene, etc.)
- phthalates (diethylhexylphthalate, dibutylphthalate, dimethylphthalate).

Human and aquatic toxicity, high volatility and high odour intensity are the main concerns associated with the use of the above-mentioned substances. Not only do water and air become contaminated by the emissions, but it is increasingly suspected that consumer health problems can be caused by remobilisation of halogenated carriers (e.g. 1,2,4-trichlorobenzene) in the treated textiles.

The hazardous carriers can be replaced by chlorine-free substances with improved toxicological and environmental characteristics. New carriers are based on benzylbenzoate and N-alkylphthalimide. Benzylbenzoate is a readily biodegradable substance while N-alkylphthalimide is bio-eliminable. Moreover, because of their low volatility, odour nuisance (especially in the workplace) is negligible. Both substances are water soluble and easy to remove at the end of the dyeing process. Dyeing is carried out at boil using 2–5% (o.w.f.) carrier concentration. A number of eco-label schemes recommended cessation of the use of organohalogen carriers.

### 16.7.2 Dyeing of polyester using supercritical fluid carbon dioxide

In this technique, a recyclable process medium ( $\text{CO}_2$ ) is used together with an efficient and minimum input of chemicals (only dyes, no auxiliaries) and energy and with minimal emissions and waste production. Supercritical  $\text{CO}_2$  can be regarded as a 'hybrid solvent' due to the fact that by simply changing the pressure or the temperature, the properties can be turned from liquid-like to gas-like without crossing a phase boundary.<sup>98</sup> Generally, the liquid-like supercritical fluids possess solvating power and the pressure increase enhances the solvent power. This property is used for the dyeing of polyester using supercritical fluid carbon dioxide. The developments in the process and its environmental aspects have been reviewed by Bach and Schollmeyer.

Dyeing in supercritical carbon dioxide has been identified as one of the best alternatives to water-based dyeing. However, this attractive concept is waiting for commercial implementation. Economical feasibility has to be determined in the future after industrial scale-up of the plant and the process, but as profit margins are becoming tighter, it seems unlikely that this process will be commercially viable in the near future. The successful commercialisation of the concept will definitely improve the environmental friendliness of dyeing by way of elimination of waste water discharges.<sup>99,100</sup>

### 16.7.3 After-treatment of polyester

A major problem in the dyeing of Polyester (PES) fibres and PES blends using disperse dyestuffs is wash fastness. In order to meet washing fastness requirements, reductive after-treatment is carried out in a fresh bath using sodium hydrosulphite and a dispersing agent in alkaline conditions at 80°C. Afterwards the bath is drained and one or two more rinsing steps under acidic pH are needed in order to remove the remaining alkali and reducing agent.

In addition to the environmental concerns involved with the use of hydrosulphite as reducing agent, this process entails three bath changes. Thus there is higher consumption of water, energy and chemicals, greater demands on time and increased levels of salt in the effluent.

Two different approaches are proposed:

1. Approach A consists of using a reducing agent based on a special short-chain sulfinic acid derivative that can be added directly in the exhausted acidic dye bath. This reducing agent is liquid and can therefore be metered automatically. Moreover, it has very low toxicity and is readily biodegradable. Since this reducing agent can be applied in the acidic pH range, significant water and energy savings (up to 40%) can be achieved.
2. Approach B consists of using disperse dyes that can be cleared in alkaline medium by hydrolytic solubilisation instead of reduction. These are azo disperse dyes containing phthalimide groups. With alkali-dischargeable dyes the use of hydrosulphite or other reducing agents can be avoided. There is the possibility of dyeing PES/cotton blends using a one-bath two-step dyeing method, as alkali-clearable dyes can be applied in the same bath with cotton reactive dyes. This brings about additional environmental benefits in terms of water and energy consumption.<sup>101,102</sup>

## 16.8 Future trends

The success of environmentally friendly dyes and dyeing processes in future will depend on the developments in new generation dyes, application methods particularly for reduction of colour and salt in the effluent, proprietary



issues related to disclosure of chemical structures of dyes and auxiliaries, reduction of impurities in commodity chemicals, automation, etc.

New generation of dyestuffs will be based on better treatability, higher exhaustion thus less colour residue in waste water, and safer intermediates, while maintaining desirable tinctorial, cost and fastness properties. The application properties of these dyes of the future should be adequate in terms of repeatability and compatibility with existing equipment. This new generation of dyes should require fewer dyeing assistants, especially salt, retarders and accelerants. Fibre reactive dyes for cotton, which are the fastest growing class of dyes over the last 20 years, are promising for this major opportunity to reduce or eliminate some of the most intractable emerging problems of colour residues in dyeing and printing waste water, massive electrolyte discharges, aquatic toxicity and elimination of low levels of metals from waste water. One approach that has been proposed is to make dyes more reactive. However, without higher affinity properties the above goals cannot be accomplished.

Another important opportunity is the development of azo dyes based on iron instead of more harmful metal ions such as cobalt, nickel, chromium, lead and zinc. This line of research has already shown promise in substituting iron for cobalt in Acid Red 182 and Acid Blue 171, and also iron for chromium in Acid Black 172. These new dyes should be non-mutagenic and of course not introduce undesirable metals in dyeing waste water.<sup>103</sup>

There is also the need to develop new application methods especially for existing fibre reactive dyes on cotton. One successful approach is pad-batch dyeing, which is well known. Other methods are also needed, especially for tubular knits and other substrates not adaptable to pad-batch dyeing. Using alternative electrolytes or other methods to control dye affinity and exhaustion via solubility control and fibre zeta potential is another opportunity which needs investigation.<sup>104-107</sup>

The incentive to establish a good pollution prevention programme is often economic. These programmes are often justified through a 'pollution prevention pays profits' type of thinking.

In addition to specialties, textiles use massive amounts of commodity chemicals, e.g. acid, alkali, salt, warp size, etc. A typical cotton production facility might use commodities that are greater than the weight of product produced. It is not unusual to find cotton dye-houses which discharge 3000 ppm of salt in the waste water. There are two needs in this area. The first challenge is to reduce the amounts of commodities, especially salt, required for dyeing. The second is to determine the trace impurities in commodities and to seek better sources of commodities, or better methods of manufacturing commodities, which reduce or eliminate offensive trace materials. Tests of textile waste water have clearly shown the presence of toxic materials which also have been detected as impurities in fibres

and chemical commodities. These toxic waste water pollutants are present in significant amounts in high volume raw materials (e.g. fibres) as well as salt and alkalis.<sup>108</sup> Equipment automation is a major focus of textile process improvement. At any international textile machinery exhibition, the companies demonstrating microprocessor controllers, chemical dispensing systems, etc. outnumber the companies showing dyeing machines. Automation can produce good results in quality, productivity and pollution reduction, because routine waste levels are decreased, cleanup is easier, mixes are made more accurately and human errors are reduced.

The need for better disclosure of chemical constitution of chemical specialities is important. The same challenge exists for dyes. In the past, dyes have been classified by chemical structure and application factors in the *Colour Index*. For non-technical business reasons, this indexing system seems to be coming to an end, due to the withdrawal of support by many of the major dyestuff companies. In the future, dyes will become more proprietary, similar to speciality products, with associated loss of information for the user. Lack of information in the future will make evaluation of pollution problems, substitutions, etc. even more difficult for textile mills because they will know less about the chemical constitution and structure of the dyes which they are using. Similarly, speciality textile processing assistants are used in large quantities with relatively little information about their pollution potential. There is a clear need for disclosure of user information, which is in a sense a business issue. The challenge is somehow to overcome the proprietary nature of specialities and globally select compatible processing assistants. The barriers to this are great, but the potential rewards of such an approach would be immense. The introduction of systems like REACH and GHS should be helpful in this respect.

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**Abstract:** This chapter reviews the chemistry and application technology of fluorescent dyes as applied to textiles. Following a brief review of the historical background, the physical principles underlying fluorescence are presented. The molecular structures of fluorescent dyes for textile applications are illustrated and discussed in terms of general structural features and the most important chemical classes. Textile applications of fluorescence, using dyes and daylight fluorescent pigments, are reviewed together with a brief overview of some important non-textile applications of fluorescent dyes. The chapter concludes with informed speculation on likely future trends in fluorescence on textiles.

**Key words:** fluorescence, dyes, daylight fluorescent pigments, carbonyl.

## 17.1 Introduction

Fluorescence involves the absorption of ultraviolet (UV) or visible light and emission of light at higher wavelengths. Fluorescent dyes are defined as compounds which both absorb and emit strongly in the visible region, and which owe their potential for application to their intense fluorescence properties. This chapter provides an overview of the chemistry and application technology of fluorescent dyes with particular reference to their use on textiles. Section 17.2 deals with the fluorescence phenomenon with some relevant historical background and a discussion of the underlying physical principles, including definitions of the terminology applied. The chemistry of fluorescent dyes, with special emphasis on those dyes suitable for textile applications, is described in Section 17.3. A review of the general structural features of molecules which give rise to fluorescence is followed by a description of the classification of fluorescent dyes according to chemical type, including carbonyl (coumarin, naphthalimide, perylene, benzanthrone, benzoxanthone and benzothioxanthone derivatives), rhodamine, methine and heterocyclic classes, with illustrations of the most important chemical structures. Section 17.4 deals specifically with the most important textile applications of fluorescence, on natural and synthetic fibres, encompassing the use of both dyes and daylight fluorescent pigments, while Section 17.5 provides a brief overview of some of the important non-textile applications



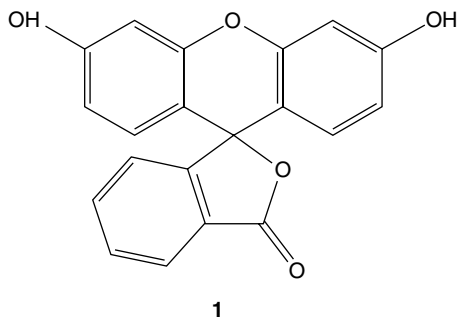
of fluorescent dyes, including lasers, defect detection and tracing, analytical and biomedical applications, solar collectors and electronic flat-screen displays. The chapter concludes in Section 17.6 with some informed speculation concerning future trends in fluorescent dyes for textiles.

## 17.2 Fluorescence

### 17.2.1 A brief historical perspective

The earliest observation of fluorescence is commonly attributed to Spanish botanist and physician Monardes who, in 1565, reported the emission of blue light from an infusion of wood (*Lignum nephriticum*) used at the time for treatment of liver and kidney ailments (Beltrami *et al.*, 1981; Harvey, 2005). The term *fluorescence* was first used by Sir George Gabriel Stokes in the mid-nineteenth century to describe the visible light emission from the mineral fluorite (calcium fluoride) when irradiated by ‘invisible’ UV light. Stokes, who was Professor of Mathematics at the University of Cambridge, made an immense lasting contribution to our current understanding of the principles of fluorescence. As an example, he established that light emitted by a fluorescent material is inevitably at longer wavelengths than the light absorbed, an observation which gave rise to the parameter which has become known as the Stokes shift, the difference between emitted and absorbed wavelengths (Harvey, 2005; Valeur, 2001).

There are several early reports of the unusual fluorescent brilliance of certain dyes applied to natural textile fibres, especially silk (Gandswandt, 1921; Hummell, 1893; Knecht *et al.*, 1910; Ramsay and Weston, 1917). The greenish-yellow fluorescein (**1**) (Fig. 17.1) and its orange to red halogenated derivatives (eosins) were among such dyes described in early literature. However, their practical use was limited by inadequate fastness properties. The structurally related brilliant bluish-red rhodamines (see Section 17.3.3) were found to perform rather better. The rhodamines have become



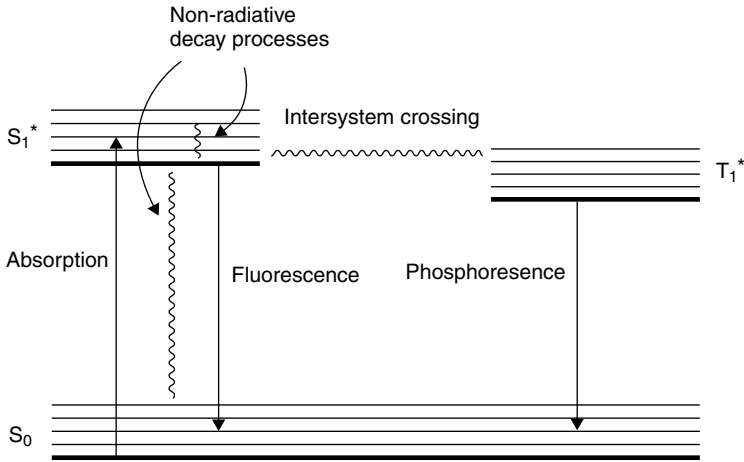
17.1 The structure of fluorescein (**1**).

established as one of the most important classes of fluorescent dyes for a wide range of applications, although they are currently not used quite so extensively on textiles as some other chemical classes. As synthetic textile fibres, notably polyester, nylon and acrylics, emerged in the mid-twentieth century and became established commodities, a range of fluorescent dyes were developed specifically for application to those fibres. Around the same period, products which have become known as *daylight fluorescent pigments* were introduced, providing a vivid brilliance of colour for a wide range of applications including printed textiles, coatings and plastics. Fluorescent dyes are also used in a diverse range of applications which specifically exploit their intense light emission properties. These functional uses of the dyes, many of which remain the subject of intense ongoing investigation, include important analytical methodologies, biological applications, for example, detection and quantification of biomolecules and diagnostics, non-destructive flaw detection, dye lasers, solar collectors and electronic display technologies.

Fluorescent dyes have been defined (Christie, 1993) as compounds which both absorb and also emit strongly in the visible region of the electromagnetic spectrum, and which owe their potential for application to their intense fluorescence properties. This specific definition excludes fluorescent brightening agents (FBAs), which absorb in the UV region and emit visible (generally blue) light. There are, however, significant similarities between FBAs and fluorescent dyes in terms, for example, of the structural features of certain chromophores and the range of applications (Barton and Davidson, 1974; Siegrist *et al.*, 1987). Fluorescent dyes are generally based structurally on very specific chemical units (see Section 17.3). Azo dyes, by far the most important chemical class of colourants for traditional textile and other applications, are in general non-fluorescent. Certain dyes from other traditional dye chemical classes, including carbonyl dyes (e.g. anthraquinones) and phthalocyanines, may exhibit a visibly detectable fluorescence which contributes positively to the brightness of colour, although the fluorescence intensity is insufficient to meet the specific definition which would allow them to be classified as fluorescent dyes.

## 17.2.2 Physical principles of fluorescence

The visual effect provided by a fluorescent dye, whether in solution or incorporated into a textile fabric, is due to a combination of two effects: the base colour due to the wavelengths of light transmitted or reflected as a result of selective light absorption, supplemented by the colour due to the wavelengths of emitted light by fluorescence. The energy transitions which occur in a molecule exhibiting fluorescence are illustrated in



17.2 Some energy transitions in a fluorescent dye.

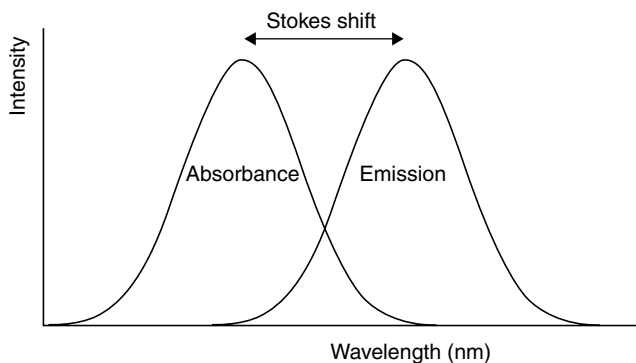
Fig. 17.2 (Guilbault, 1990; Krasovitskii and Bolotin, 1988; Lakovicz, 2006; Murrel, 1971; Valeur, 2001). When a molecule absorbs light, it does so in discrete amounts of energy, termed *quanta*. It is thus excited from the lowest vibrational level in its ground state ( $S_0$ ) (its most stable state), to a range of vibrational levels in the first excited singlet state ( $S_1^*$ ). In the case of organic fluorescent dyes, this is generally a  $\pi \rightarrow \pi^*$  electronic transition which occurs very fast, in about  $10^{-15}$  s (femtoseconds). The energy ( $\Delta E$ ) of this electronic energy transition, the difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), determines the colour due to light absorption in terms of the absorption wavelength ( $\lambda$ ), in accordance with Planck's relationship (Equation [17.1]).

$$\Delta E = h\nu = hc/\lambda \quad [17.1]$$

where  $h$  is Planck's constant,  $\nu$  and  $\lambda$  are, respectively, the frequency and wavelength of the light absorbed and  $c$  is the speed of light. Because of the inverse relationship between  $\Delta E$  and  $\lambda$ , the higher the energy difference ( $\Delta E$ ), the shorter the wavelength ( $\lambda$ ) of absorbed light. During the time the molecule spends in the excited state, energy is dissipated from the higher vibrational levels (*vibrational relaxation* or *internal conversion*) until the lowest vibrational level is attained, typically within a timeframe of  $10^{-10}$ – $10^{-12}$  s (picoseconds). Fluorescence occurs if the molecule then emits light as it reverts from this level to various vibrational levels in the ground state ( $S_1^* \rightarrow S_0$ ), which occurs within a timeframe of  $10^{-7}$ – $10^{-9}$  s (nanoseconds). Non-radiative processes also cause dissipation of energy from the

excited state, either as heat or by transfer of energy in collision with other molecules, the latter effect known as *quenching*. The extent to which these processes compete with fluorescence determines its intensity. In reality, most commercial dyes do not exhibit significant fluorescence. The quenching phenomenon means that the fluorescence intensity exhibited by a dye is influenced profoundly by its environment. Factors which influence fluorescence quenching include the chemical nature of the solvent or matrix into which the dye is incorporated, its concentration and purity, and the presence of other species. For example, molecular oxygen and certain ions can cause significant fluorescence quenching. Another process which may occur in this photoinitiated process is *intersystem crossing* from the singlet excited state ( $S_1^*$ ) to an excited triplet state ( $T_1^*$ ). Subsequent emission of light from the triplet state ( $T_1^* \rightarrow S_0$ ) is termed *phosphorescence*, a much longer lasting (glow in the dark) light emission phenomenon ( $10^{-1}$ – $10^2$  s).

Because vibrational energy is lost in the excited state before fluorescence occurs, and in accordance with the inverse relationship between electronic transition energy ( $\Delta E$ ) and wavelength ( $\lambda$ ) as described by Planck's relationship, emission inevitably occurs at longer wavelengths than absorption. The absorption and emission spectra of a fluorescent dye often approximate to mirror images of one another as illustrated in Fig. 17.3. The difference between the emission and absorption wavelength maxima is referred to as the *Stokes shift*. The intensity of light emission from a fluorescent dye is characterised by its *quantum yield* ( $\eta$ ), which is defined as the ratio of the emitted quanta to the absorbed quanta of light. Thus, a non-fluorescent material has a quantum yield of 0, while a perfect fluorescer would give a quantum yield of 1. With some fluorescent dyes, and in ideal circumstances, the quantum yield may approach unity.



17.3 Absorption and emission spectra of a typical yellow fluorescent dye.

## 17.3 Chemical types of fluorescent dye

### 17.3.1 General structural features

Fluorescent dyes, by definition, are required to absorb in the visible region and to exhibit intense fluorescent emission (Christie, 1993). Other desirable characteristics of the dyes, such as fastness properties (for example to light, washing and other agencies in the case of textile dyes), functional properties and toxicological issues, are dictated by the nature of particular applications and the conditions to which the dyes are likely to be exposed. The relationship between the colour of dyes derived from light absorption and their molecular structures is generally well understood (Gordon and Gregory, 1983). Quantitative approaches to the calculation of the colour properties of dyes have become well established, mostly as a result of the application of molecular orbital (MO) theory using computer-aided quantum mechanical approaches, such as the PPP MO, CNDO and ZINDO methods (El-Shafei *et al.*, 2001; Griffiths, 1981). Absorption  $\lambda_{\max}$  values may be routinely calculated, and molar extinction coefficients may be estimated from a calculated parameter known as the oscillator strength. Some broad principles underlying the relationship between the molecular structure and the light emission properties of dyes have been established, although arguably less rigorously, both qualitatively and quantitatively, than is the case with absorption. The Stokes shift is an important parameter in fluorescent dye applications. For most fluorescent dyes, the Stokes shift is generally around 50–70 nm. As an example, a dye absorbing light at around 430 nm will emit around 480–500 nm and will therefore appear yellow with a green fluorescence. As a rough guide based on this principle, FBAs absorbing below 380 nm will emit blue light (420–450 nm), yellow dyes will emit green (480–500 nm), red dyes will emit yellow, orange or red (540–580 nm) and blue dyes will emit red light (660–700 nm) or in the near infrared region. In some functional applications, a larger Stokes shift is desirable to minimise the overlap between the absorption and emission spectra. A semi-empirical approach to the calculation of Stokes shifts in fluorescent dyes has been reported which uses a modification of the PPP MO method (Fabian, 1985; Lubai *et al.*, 1989; Xuhong *et al.*, 1989). Initially, a conventional PPP MO calculation, using standard ground state molecular geometries and resonance integrals, is used to calculate an absorption  $\lambda_{\max}$  value. From the calculated first excited state  $\pi$ -bond orders, excited state geometries and resonance integrals are derived. Subsequent calculations are carried out using these new parameters, iteratively, until convergence is achieved. The resulting  $\lambda_{\max}$  value is equated to the fluorescence maximum and hence the Stokes shift is obtained as the difference between this value and the original result. While the method lacks rigorous theoretical justification, good correlations have been reported for a range of fluorescent dye chemical classes.

Some general principles with regard to the relationship between the molecular structure of dyes and their fluorescence intensity, as determined by quantum yields, are recognised (Christie 1993; Hunger, 2003). Fluorescent dyes are generally extended conjugated aromatic systems, often containing multiple fused rings. An important molecular feature commonly associated with high fluorescence quantum yields is structural rigidity. In a rigid molecule, loss of energy from excited states by intramolecular thermal motion is minimised, favouring fluorescent emission over non-radiative energy loss. The reduction of fluorescence intensity in molecules with less structural rigidity has been termed, by an appropriate mechanical analogy, the *loose-bolt effect*. Azo dyes, which contain two aromatic systems linked by the azo ( $-\text{N}=\text{N}-$ ) group, are generally non-fluorescent (Christie, 2001, Chapter 3). The molecular arrangement in azo dyes is inherently less rigid than fused polycyclic systems, allowing a degree of rotation around the azo linkage. Similarly, it is recognised that the presence of the nitro ( $-\text{NO}_2$ ) group, which can undergo relatively free rotation, commonly suppresses fluorescence. However, the validity of classical explanations based on molecular rigidity alone has been questioned, at least in part because exceptions are fairly commonly encountered and more complex arguments associated with the nature of excited states structures and the charge transfer electronic transitions which are involved, including for example the role of non-bonding electrons, have been proposed. In spite of containing planar aromatic ring systems, highly fluorescent dye molecules often also contain structural features which confer a considerable degree of non-planarity. Planar molecules have a tendency to aggregate, in extreme cases becoming pigmentary, and dissipate excited state energy through relaxation processes which involve intermolecular interactions. The classical example of a fluorescent dye, fluorescein (**1**) (Fig. 17.1), provides an example of a rigid yet non-planar molecular structure which leads to high fluorescence intensity. Another molecular feature recognised as generally leading to reduced fluorescence is the presence of atoms of higher atomic number, such as bromine and iodine, a phenomenon referred to as the *heavy atom effect*. An important challenge which would assist the design of new fluorescent dyes is the development of a reliable quantitative method for the calculation of quantum yields. Such methods would probably require a theoretical approach to the relative rates of fluorescence emission and competing non-radiative deactivation processes from the excited state. A significant difficulty inherent in developing and verifying such an approach is the profound influence of environmental effects, such as the nature of the solvent, dye concentration and temperature, on fluorescence emission spectra.

Intense fluorescence in dyes is commonly associated with the presence of certain specific, identifiable structural units. These units form the basis of the classification of chemical types of fluorescent dyes which is described

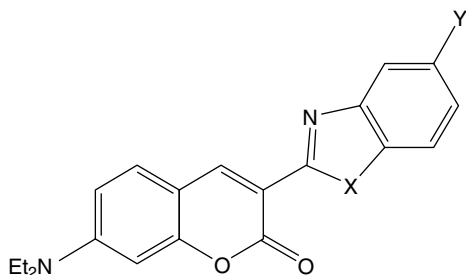
in the following sections of this chapter. A wide variety of chemical types of fluorescent dyes is available commercially. This is especially the case for fluorophores designed for biological applications which are often sold in tiny quantities at highly inflated prices. This chapter, however, is focused on the principal structural types which can find use in textiles.

### 17.3.2 Fluorescent carbonyl dyes

The most important group of fluorescent dyes for textile applications contain the carbonyl group as an essential structural feature (the chromophore) (Christie, 2001, Chapter 4). These dyes are classified together in this section.

#### *Coumarins*

Coumarin derivatives provide the most important industrial fluorescent dyes. Fluorescent coumarins are known which absorb and emit in most parts of the visible spectrum, although most commercial products are yellow with a green fluorescence. FBAs based on coumarins are also used commercially. The coumarin dyes invariably contain an electron-releasing substituent, most commonly the diethylamino group, in the 7-position, and electron-withdrawing substituents in the 3-position. The coumarins are thus typical donor-acceptor dyes (Christie and Lui, 2000). The most widely used dyes contain a benzimidazolyl (**2a**), benzoxazolyl (**2b**, **2d**, **2e**) or benzothiazolyl (**2c**) group as the acceptor in the 3-position (Fig. 17.4). This group provides important disperse dyes which allow synthetic fibres, especially polyester, to



**2**

2a: X = NH; Y = H

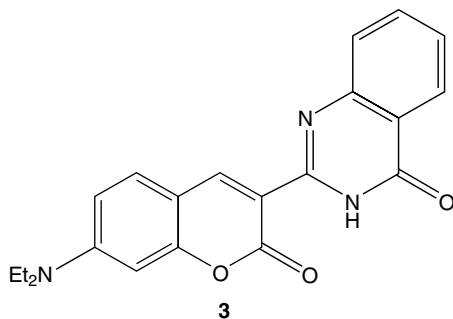
2b: X = O; Y = H

2c: X = S; Y = H

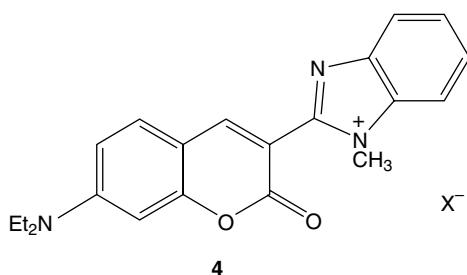
2d: X = O; Y = CH<sub>3</sub>

2e: X = O; Y = Cl

17.4 General structure (**2**) of the most common coumarin fluorescent dyes.



175 The structure of coumarin fluorescent dye, C.I. Disperse Yellow 186 (**3**).



176 The structure of C.I. Basic Yellow 40 (**4**).

be dyed in brilliant fluorescent greenish-yellow shades. Dyes with alternative heterocyclic substituents in the 3-position are known, for example C.I. Disperse Yellow 186 (**3**) (Fig. 17.5).

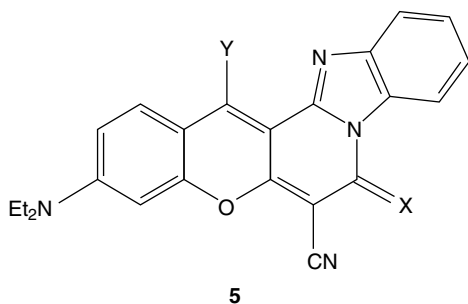
Benzazolyl-substituted coumarins can also be converted into water-soluble cationic dyes by alkylation of theazole ring nitrogen atoms. An important product is C.I. Basic Yellow 40 (**4**) (Fig. 17.6), a greenish-yellow dye which finds applications in acrylic fibres and in daylight fluorescent pigments.

An interesting group of coumarin dyes, as illustrated in Fig. 17.7, includes dyes **5a** and **5b** which absorb and emit at longer wavelengths, as a result of additional ring-formation and enhanced electron-withdrawing character. These are fluorescent red dyes suitable for application to polyester. The cyano derivative **5c** is reported as a greenish-blue dye exhibiting red fluorescence (absorption maximum at 630 nm, emission maximum at 668 nm) (Moeckli, 1980). Dyes exhibiting such colouristics are quite unusual.

### *Naphthalimides*

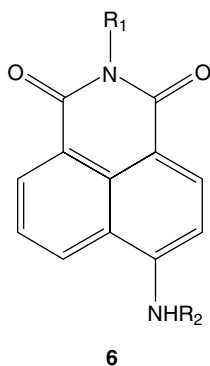
Fluorescent materials based on the imides of naphthalic acid (naphthalene-1,8-dicarboxylic acid) are well known. Strong fluorescence is observed when





- 5a: X = O; Y = H  
 5b: X = NH; Y = H  
 5c: X = NH; Y = CN

### 17.7 Fused-ring fluorescent coumarin dyes (5).

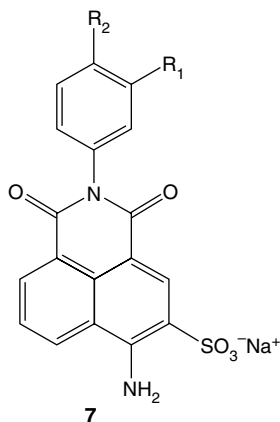
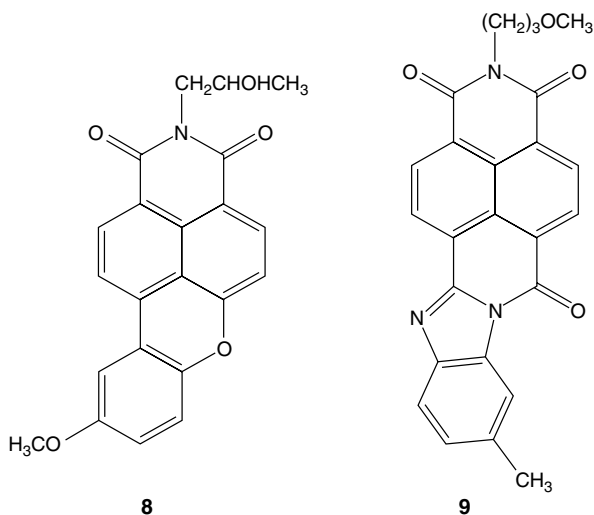


- 6a: R<sub>1</sub> = 2,4-dimethylphenyl; R<sub>2</sub> = H  
 6b: R<sub>1</sub> = R<sub>2</sub> = (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>

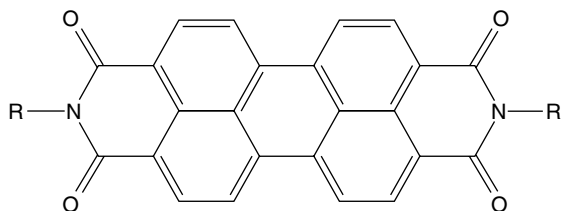
### 17.8 Structures of aminonaphthalimide fluorescent dyes (6).

there is an electron-donating group in the 4(5)-position, in which case the absorption and emission properties are associated with charge transfer involving the donor group and the electron-withdrawing peri-carbonyl groups. C.I. Disperse Yellow 11 (**6a**), which contains an unsubstituted amino group and an aryl substituent on the imide nitrogen, is a long-established fluorescent yellow dye although with only moderate light fastness. C.I. Solvent Yellow 43 (**6b**), containing n-butyl groups on both the imide and amine nitrogens, is appreciably redder and stronger but exhibits poorer light stability. The structures of these dyes are given in Fig. 17.8.

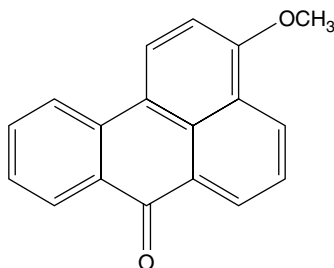
A number of water-soluble naphthalimide dyes, including the anionic dyes C.I. Acid Yellow 7 (**7a**) and C.I. Mordant Yellow 33 (**7b**), have been

7a:  $R_1 = H$ ;  $R_2 = CH_3$ 7b:  $R_1 = CO_2H$ ;  $R_2 = OH$ 7c:  $R_1 = SO_2CH_2CH_2OSO_3^-Na^+$ ;  $R_2 = OCH_3$ 17.9 Water-soluble aminonaphthalimide dyes (**7**).17.10 Fused-ring naphthalimide dyes (**8**) and (**9**).

used as dyes for silk and may also be used in non-destructive flaw detection. Fluorescent yellow reactive dyes for cellulosic fibres, such as **7c**, have been described. The structures of these dyes are given in Fig. 17.9. C.I. Disperse Yellow 199 (**8**) and Orange 32 (**9**) are examples of naphthalimides in which the donor group is built into a fused heterocyclic system (Fig. 17.10).

**10**

17.11 The general structure of perylene fluorescent dyes (**10**).

**11**

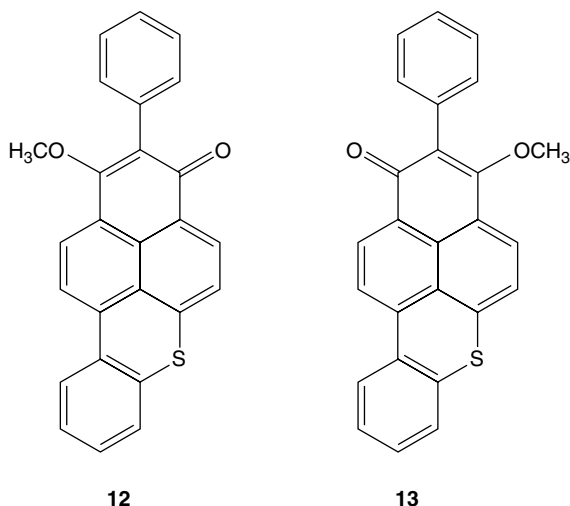
17.12 The structure of 3-methoxybenzanthrone (**11**).

### *Perylenes*

The most important fluorescent perylene dyes are a range of N,N-disubstituted diimides of perylene-3,4,9,10-tetracarboxylic acid (**10**) (Fig. 17.11) which provide intense orange to red fluorescent colours in polymers. The imide nitrogen atoms are commonly substituted (R) with aryl or bulky alkyl groups such as *t*-butyl. These perylene dyes are of special interest because they provide bright colours with very high fluorescence efficiency while at the same time they are extremely stable towards light and heat and are resistant to chemical attack. For these reasons, they are attractive materials for the colouration of thermoplastics, and they are frequently the materials of choice for functional applications such as liquid crystal displays and solar-energy collection where durability is of prime importance. They are not especially suited to textile applications.

### *Benzanthrone derivatives*

The longest-established fluorescent benzanthrone dye is the 3-methoxy derivative (**11**) (C.I. Disperse Yellow 13) (Fig. 17.12) which exhibits



17.13 The isomers (12) and (13) of C.I. Disperse Red 303.

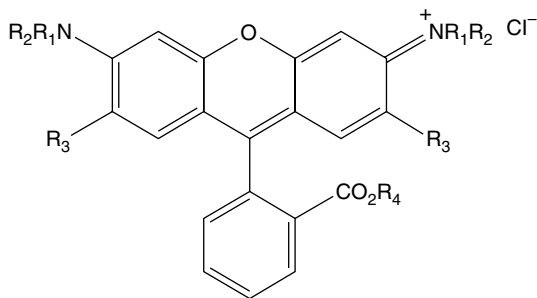
yellow-green fluorescence (Ellis, 1941). This dye is relatively inexpensive but suffers from the disadvantage of a rather low quantum yield. However, the fluorescence intensity can increase in the resin systems used in daylight fluorescence pigments, an effect attributed to intermolecular hydrogen-bonding between dye and resin molecules.

#### *Benzoxanthenes and benzothioxanthenes*

A range of dyes based on the benzoxanthone and the benzothioxanthone systems were extensively investigated by Hoechst during the 1970s as brilliant fluorescent and lightfast disperse dyes for polyester. C.I. Disperse Red 303, a fluorescent yellowish-red, has been disclosed as a mixture of the isomers (12) and (13), as illustrated in Fig. 17.13 (Ayyanger and Srinivasin, 1985).

### 17.3.3 Rhodamines

Triarylmethine (or arylcarbonium) dyes do not as a rule exhibit strong fluorescence (Christie 2001, Chapter 5). However, a number of structurally related dyes which contain a pyran ring are strongly fluorescent, because of the enhanced molecular rigidity due to the oxygen bridge. This group of compounds includes the 'classic' luminophors fluorescein (1) (Fig. 17.1) and the rhodamines (Fig. 17.14). Fluorescein is no longer significant as a textile dye but is used in hydrogeological tracing and in

**14**

14a:  $R_1 = R_2 = C_2H_5$ ;  $R_3 = R_4 = H$

14b:  $R_1 = H$ ;  $R_2 = R_4 = C_2H_5$ ;  $R_3 = CH_3$

17.14 The structure of rhodamine dyes (**14**).

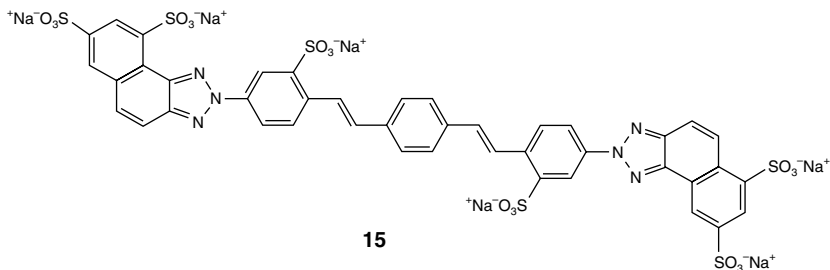
analytical and biological applications. However, rhodamines are of major commercial importance as intensely fluorescing red to violet materials. Of particular interest are rhodamine B (**14a**) (C.I. Basic Violet 10) and rhodamine 6G (**14b**) (C.I. Basic Red 1) both of which find a wide variety of traditional and functional applications. Rhodamine 6G is an important red dye for daylight fluorescent pigments and was one of the first to be used in dye lasers. Rhodamines now find little use on textiles because of their limited stability and a tendency to reduce in fluorescence intensity due to quenching effects.

### 17.3.4 Methine fluorescent dyes

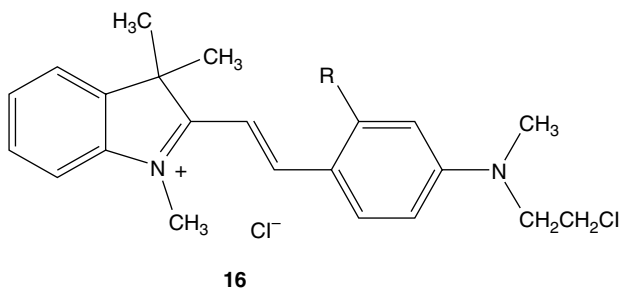
Many polycyclic aromatic hydrocarbons display strong fluorescence in the visible region, but their commercial exploitation is restricted by synthetic difficulties and their potentially carcinogenic nature. Some triazole derivatives of stilbene are fluorescent direct dyes suitable for application to cellulosic fibres, an example being compound **15**, C.I. Direct Yellow 96 (Fig. 17.15). Certain cationic methine dyes, such as C.I. Basic Red 13 (**16a**) and C.I. Basic Violet 7 (**16b**) (Fig. 17.16) may be used to dye acrylic fibres.

### 17.3.5 Miscellaneous fluorescent dyes

C.I. Disperse Yellow 139 (**17**) is a structurally more complex heterocyclic dye which provides bright greenish-yellow shades on polyester, cellulose



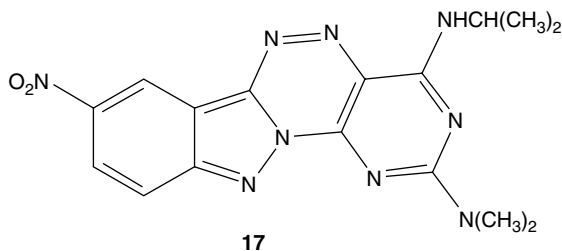
1715 The structure of stilbene fluorescent dye (15).



16a: R = H

16b: R = CH<sub>3</sub>

1716 Fluorescent cationic methine dyes (16).



1717 The structure of heterocyclic fluorescent dye (17).

acetate and polyamides with excellent fastness to light, washing and sublimation (Ayyanger and Srinivasin, 1985). There are a large number of other chemical types of fluorescent dyes which are not included in this chapter because they are not of interest for textiles (Christie, 1993; Mama, 1999).

## 17.4 Textile applications of fluorescent dyes

The applications of fluorescent textiles are associated with their ability to attract attention, because of the remarkable vivid brilliance of the colours which results from the extra glow of emitted fluorescent light (Higgins and Towns, 2003). Fluorescent fabrics may be used for specific aesthetic and fashion purposes, the eye-catching bright colours providing unique creative opportunities for the textile and garment designer. They are also used for functional reasons, assuming special importance in leisurewear, sportswear and workwear. Wearing garments with fluorescent colours is desirable when safety is paramount in the workplace, for example as used by police, fire-fighters and other emergency services personnel, and construction workers who require visibility in their work surroundings. Fluorescent sportswear and leisurewear are also important for athletes and cyclists, especially when they are exercising in a dimly lit environment. Fluorescence may also be used in certain non-traditional textile applications, a familiar example being yellow tennis balls. Fluorescence may be introduced into textiles either by traditional dyeing processes with the dye application classes appropriate to the textile material, or by printing with daylight fluorescent pigments. In both of these cases, the colour is derived from the use of fluorescent dyes. It is worth repeating that the review of the dyes given in the previous section of this chapter is mostly focused on those dyes most commonly applied to textiles, and the reader is directed back to that section for the specific chemical structures.

### 17.4.1 Fluorescent dyes for textiles

Fluorescent dyes are not considered by the *Colour Index* as a separate, identifiable dye application class. Instead, the commercially important textile fluorescent dyes, which are relatively few in number, are distributed among the traditional application classes. Thus the methods used to dye the fibres, yarns or fabrics are characteristic of the particular class, details of which the reader will find in the relevant chapters of this textbook. The earliest commercial exploitation of fluorescent dyes was the use of rhodamines and related products to dye silk with unusually brilliant colours. Only a very limited number of fluorescent dyes reported as suitable for application to natural protein and cellulosic fibres are described in the *Colour Index*. C.I. Acid Yellow 7 (**7a**) and C.I. Direct Yellow 96 (**15**) are well-established dyes. However, they are not extensively used on textiles, one reason being inferior light fastness. They are more suited to applications such as hydrogeological tracing. C.I. Acid Yellow 250 (structure not disclosed) is reported as useful for dyeing the felt for yellow tennis balls. There is one reactive dye of the vinylsulphone type (C.I. Reactive Yellow 78, **7c**) reported in the

*Colour Index*, although described as having no current commercial supplier. Interestingly, a fluorescent dye, Remazol Luminous Yellow FL, was introduced by DyStar in 2002. It was claimed as the first fluorescent reactive dye for cellulosic fibres suitable for high-visibility workwear and sportswear applications. It is reported as being compatible in application with other Remazol reactive dyes, and especially useful for dyeing fluorescent yellow shades on blends of cellulose with polyester and polyamides (Michel, 2002).

Fluorescent dyes are of much greater importance for application to synthetic fibres such as polyester, polyamides and polyacrylonitrile, sometimes also in conjunction with elastane fibres. The most important textile applications are on polyester and thus the most important fluorescent textile dyes are from the disperse dye class. Fluorescent disperse dyes are also used, but to a lesser extent, on polyamides and cellulose acetates. Most of the commercial dyes are yellow, providing the very familiar greenish-yellow fluorescent colours very commonly encountered on garments worn for safety purposes. There are also a number of oranges and reds. The important fluorescent coumarin dyes include C.I. Disperse Yellows 82 (**2a**), 184 (**2d**), 186 (**3**) and 232 (**2d**), and C.I. Disperse Reds 277 (**5a**) and 374 (**5b**). An interesting publication analyses the market for fluorescent dyes in Poland and assesses the suitability of the commercially available yellow dyes to meet the requirements of the European standard (EN 471:1997) for high-visibility 'warning' clothing (Szuster *et al.*, 2004). The paper also describes an analytical investigation which suggests that C.I. Disperse Yellow 184:1 is chemically identical to C.I. Disperse Yellow 232 (**2d**). This is a particularly important commercial dye, providing brilliant greenish-yellow shades on polyester with good fastness to light, sublimation and washing (Ayyanger *et al.*, 1990). Apparently, dye **3**, usually referred to as C.I. Disperse Yellow 186, also has a duplicate designation as C.I. Disperse Yellow 202. The range of fluorescent dyes disclosed in the *Colour Index* also includes the aminonaphthalimides, C.I. Disperse Yellows 11 (**6a**) and 199 (**8**), and Orange 32 (**9**), the benzothioxanthone, C.I. Disperse Reds 303 (mixture of **12** and **13**) and the heterocyclic C.I. Disperse Yellow 139 (**17**). There are a number of water-soluble fluorescent cationic dyes of commercial significance for application to acrylic fibres, including the coumarin C.I. Basic Yellow 40 (**6a**) and the methine dyes C.I. Basic Red 13 (**16a**) and C.I. Basic Violet 7 (**16b**). Fluorescent disperse dyes on polyester and cationic dyes on acrylic fibres show technical performance characteristics typical of the dye application class. The commercial fluorescent dyes recommended for textiles are often criticised for light fastness properties which are unable to meet the standards required by more demanding applications. However, this feature can be improved by judicious use of light stabilising additives such as UV absorbers.



## 17.4.2 Daylight fluorescent pigments

The largest industrial market for fluorescent dyes is for use in daylight fluorescent pigments (Moore, 1983). These pigments may be applied to textiles, dispersed into traditional aqueous pigment binder formulations, by screen printing and in this way they are potentially applicable to any fabric in the same way as normal coloured pigments. They are referred to as pigments because they are used as solid dispersions in a fine particulate form. They consist of fluorescent dyes dissolved in a transparent, colourless solid polymer in a fine particle size form and in this way they are chemically different from traditional pigments. The polymers in which the dyes form a solid solution play a critical role. They must be good solvents for the dyes, and provide high solvent resistance and thermal stability. Traditionally, daylight fluorescent pigments have been based on a thermoset polymeric toluene-sulphonamide-melamine-formaldehyde resin matrix. However, there is an increasing trend towards the use of 'non-formaldehyde' thermoplastic polymers based on polyurethane, polyamide or polyester resins. Fluorescent dyes most commonly used in the pigments are the yellow benzazolylicoumarins **2a**, **2d** and **3**, aminonaphthalimides, notably compound **6a**, and the red to violet rhodamines **14a** and **14b**. For blues and greens, copper phthalocyanine pigments are commonly used as toners. A significant issue with many fluorescent pigments is the quenching of the fluorescence as the concentration of the dye in the resin is increased. This is particularly significant with the rhodamines which exhibit considerable concentration quenching above about 1%. Yellow dyes, on the other hand, may be used to 5 or even 10% in certain matrices before an excessive dulling effect, characteristic of this type of quenching, occurs. In contrast, mixtures of certain dyes may produce a fluorescence more brilliant than one dye alone, as a result of transfer of energy from one dye to another. In the same way certain FBAs may act as sensitisers enhancing the fluorescence yield from yellow dyes.

Daylight fluorescent pigments are used widely in non-textile applications for their high visual impact, including printing inks, for example in advertising, posters, magazines and supermarket packaging, coatings applications especially where safety is an important feature such as fire-engines, ambulances, rescue vehicles and for the marking of military aircraft, and in a wide range of plastic products such as toys, bottles and other containers. The light fastness of daylight fluorescent pigments is generally inferior to that of traditional coloured high performance organic pigments, and this limits to a certain extent their use in exterior applications. Nevertheless, careful selection of the resin matrix, the use of light stabilising additives in the pigments, or the use of UV-absorbing overlayers can produce a fluorescent colour with reasonable light stability.

## 17.5 Other applications of fluorescent dyes

There are many other applications of fluorescent dyes outwith textiles, as functional dyes where their intense fluorescence properties are arguably more important than the specific colours which they provide. A brief overview of these applications is presented here, not only for general interest but also because it is entirely conceivable that the emerging field of smart and intelligent textiles may well make use of some of these functional applications of fluorescent dyes in the future (Tao, 2001).

### 17.5.1 Dyes for lasers

Traditional inorganic lasers operate in the ultraviolet, visible and infrared regions but suffer from the drawback that they emit at only a few selected wavelengths and in very narrow bands. In contrast, dye lasers emit a broad band, offering the advantage of tunability over a wide wavelength range. In dye lasers, fluorescent dyes operate by absorbing a quantum of light, thus being promoted from the ground state,  $S_0$ , to higher sublevels of the first excited state,  $S_1^*$ . Lasing occurs when incident radiation interacts with the dye molecule in its excited state, stimulating the molecule to decay to the ground state by fluorescent emission. For this lasing effect, the dye molecules must exist predominantly in the excited state. The population inversion required is achieved by pumping the system with a powerful inorganic laser. In contrast to spontaneous emission, the stimulated emission from dye lasers is coherent (same phase and polarisation) and of high intensity. Although major developments in solid-state and semi-conducting lasers have gradually displaced dye lasers from their previous pre-eminent position, dye lasers still find niche applications in communication technology, microsurgery, spectroscopy and microanalysis (Brackmann, 2000).

### 17.5.2 Defect detection and tracing

The timely and reliable detection of defects in components and assemblies in equipment operating under heavy-duty conditions, for example in aviation and spacecraft, is clearly of critical importance. Fluorescent dyes may be used non-destructively for the inspection of materials by enhancing the contrast of tiny cracks and other defects which are not detectable with the naked eye. A fluorescent dye dissolved in a penetrant liquid shows up surface cracks in articles made from metal, glass, ceramics, plastics and other materials by fluorescing brightly against the non-luminescent background. In related applications in geology and hydrogeology, fluorescent dyes are used to track water currents. Highly fluorescing, low cost dyes such as fluorescein, rhodamines and water-soluble coumarin and aminonaphthalimide dyes are used.

### 17.5.3 Analytical, biological and medical applications

The use of fluorescent reagents in chemical analytical methodology is long established (Guilbault, 1990; Krasovitskii and Bolotin, 1988). Fluorescent dyes have been used extensively as reagents in quantitative fluorimetric determinations and as fluorescent indicators. Fluorimetric techniques are characterised by the simplicity of the instrumentation and high sensitivity, which allows accurate quantitative determinations of trace amounts of materials. The techniques rely on the interaction of a fluorescent dye with an analyte to cause a change in the fluorescence properties, commonly an attenuation of the fluorescence intensity, which may be used to measure the concentration of the analyte. These principles are employed in optical sensors in which fluorescence properties of a dye change in a measurable way related to the concentration of the analyte in question. The sensing element containing the dye is immobilised in a device, commonly employing fibre-optic technology, which enables measurement, manipulation and interpretation of the data and provides a read-out of the property being measured (McDonagh *et al.*, 2008; Thomson, 2006). Textile-based optical pH sensors have been proposed, using a pH sensitive fluorescent dye immobilised on viscose fabrics (Staneva and Betcheva, 2007; Staneva *et al.*, 2006).

The use of fluorescent dyes in biology and medicine is an immense field which continues to grow year by year. In terms of the chemistry of the dyes, it is a highly specialised area which sometimes involves well-established fluorescent dyes but frequently makes use of coloured fluorescent compounds synthesised for specific purposes. A general literature search on the topic of fluorescent dyes illustrates that there are far more publications on biomedical applications of these materials than any other (Mason, 1999; Jameson and Reinhardt, 1989; Thomson, 2006). The methods which use fluorescent dyes, commonly derived from their use in chemical analyses, provide high specificity and sensitivity. Fluorescent dyes are used as biological probes which bind to substances, tissue, cells or micro-organisms and may be subsequently detected by fluorimetric or microscopic techniques to determine quantitatively a substance present in a biological substrate at very low concentrations. Fluorescent probes are capable of detecting, identifying and quantifying biomolecules, such as antibodies, proteins, lipids and polysaccharides in cells. They are also used to decode cell components (DNA, RNA, proteins and enzymes) (Ranasinghe and Brown, 2005) and to probe cell structures and functions, often for diagnostic purposes. Variation in the emission characteristics of the bound fluorescent dye are indicative of changes in the conformation of biomolecules, and also the nature of their environment providing a useful tool in the investigation of

biological activity and the mechanism of biological reactions. This technology has been incorporated into practical devices for biomedical applications, including optical chemical sensors (e.g. for oxygen, carbon dioxide, pH and metal ions), optical biosensors (e.g. for enzymes, glucose, antibodies and DNA) (Borisov and Wolfbeis, 2008) and optical sensors of cell temperatures (Gota *et al.*, 2009).

#### 17.5.4 Solar collectors

The principal advantages of using solar energy to generate electricity are obvious. It utilises a non-diminishing energy source and suffers little from the global environmental problems inherent in energy generation by nuclear fission or by the combustion of fossil fuels. However, a deficiency of conventional silicon solar cells is their low efficiency, particularly at lower wavelengths in the UV and visible region. Solar collectors utilise the ability of fluorescent dyes to absorb lower wavelengths of light and to re-emit the energy at higher wavelengths to which the solar cells are more sensitive. In practice, solar collectors contain the dye in a thin sheet of plastic, usually polymethylmethacrylate, whose faces and edges are mirrored to channel the emitted radiation by internal reflection to the edge of the sheet containing the solar cell. The dyes require a high fluorescence quantum yield and high photostability. Coumarins and perylenes are important classes for these applications. Preliminary research has been reported on textile-based solar light collectors in which the fibres are coated with a thin layer containing the fluorescent dye, and this may contribute towards the aim to develop smart textiles with the capacity to use solar energy as a power source (Bahners *et al.*, 2008).

#### 17.5.5 Electroluminescence

Electroluminescence involves the conversion of electrical energy into non-thermal emitted light. Recent years have seen immense advances in electroluminescent materials for use in new and emerging technologies which may well revolutionise illumination and flat-screen display technologies. Although it is a luminescence phenomenon that is distinct from fluorescence, certain devices based on electroluminescence employ fluorescent dyes as an essential component. Of particular importance are organic light emitting diodes (OLEDs), which can be used as white light sources or in flat-screen displays. OLEDs are complex multilayer electronic devices which use fluorescent dyes to provide the source of the RGB pixelated colours in the emitter layer of multicolour displays.

## 17.6 Future trends

In common with most textile dyes, the manufacturers of commercial fluorescent dyes for textiles are now mostly located in Asia, principally India and China, although there are a few remaining important Western manufacturers of the dyes and of daylight fluorescent pigments. Fluorescent dyes adopt a unique niche position in textiles, used principally where the eye-catching high visibility that they provide is of paramount importance. Based on the likelihood that leisurewear and sportswear will continue as a growth industry sector and also because of growing safety awareness worldwide increasing the demand for protective workwear, the use of fluorescent dyes and daylight fluorescent pigments in textiles may well grow steadily into the future. The increasingly important functional uses of fluorescent dyes, for example in solar-energy conversion technologies, analytical and biomedical applications, illumination and display devices, are certain to continue to attract intense interest from academic and industrial researchers. As highlighted in a few examples of recent research reports described in the previous section of this chapter, it is conceivable that functional fluorescent dyes will ultimately find applications in smart textiles, if that predicted revolution materialises.

Colour measurement based on reflectance spectrophotometry has become an indispensable tool for the characterisation of coloured textile surfaces. Measurement of fluorescent textiles, of importance for dye recipe prediction to provide fluorescent colours and to predict the effect of laundering with detergent formulations containing FBAs, presents difficulties because in addition to reflected light there is fluorescence emission, the intensity of which depends on a number of instrumental factors (Springsteen, 1999a). One factor is the geometric configuration of the illumination and viewing in the spectrophotometer. The C.I.E. has defined four illuminating/viewing geometries:  $0^\circ/45^\circ$ ,  $45^\circ/0^\circ$ ,  $0^\circ/d$  and  $d/0^\circ$ . Many commercial spectrophotometers employ the  $0^\circ/d$  geometry, but this is not especially suitable for the measurement of fluorescent samples because, when the sample is illuminated, the emission becomes part of the diffuse illumination, essentially acting as secondary illumination. For this reason, instruments with either the  $0^\circ/45^\circ$  or the  $45^\circ/0^\circ$  geometries are preferred. A second factor is the light source used in the instrument. The intensity of fluorescence emission is proportional to the intensity of the illumination and is also influenced by the spectral power distribution. Both of these factors can vary between instruments and even within a single instrument depending on the age of the lamp and the length of time for which the instrument has been switched on. The spectrophotometer actually measures the spectral radiance factor,  $\beta T, \lambda$ , which is the sum of the reflected radiance,  $\beta R, \lambda$  and the luminescent radiance,  $\beta L, \lambda$ . The measured  $\beta T, \lambda$  values can be well over 100%, at wavelengths where

there is significant fluorescence. To overcome such problems, manufacturers incorporate filters that can modulate the intensity of the light beam. By comparing the measured values of  $\beta T, \lambda$  values of a set of fluorescent standards with the specified correct values, filters can be introduced so that the correct  $\beta T, \lambda$  values of the samples are obtained. However, while such standards are available, they have a limited lifetime after which they must be replaced. Accurate characterisation of a fluorescent surface requires a bispectral instrument which irradiates samples with discrete wavelengths throughout the spectral range and simultaneously measures the complete reflectance spectrum at each wavelength. To address this issue, bispectral fluorescence spectrophotometers have been developed with two monochromators, one between the light source and the sample and one between the sample and the detector (Aspland, 2000). Such bispectral instruments are currently more expensive than traditional spectrophotometers but this situation may change in the future. For those laboratories which use single monochromator instruments, the development of a set of stable fluorescent colour standards would assist in removing the uncertainty of the accuracy of the colourimetric values obtained (Springsteen, 1999b).

The molecular basis of fluorescence, and the ability to predict fluorescence properties of dyes, remains an incompletely understood science. A higher level of attention to studies of the relationship between molecular structure and fluorescence, especially in a quantitative sense, would assist in the future design and development of new fluorescent dyes for improved performance, especially for emerging technologies based on functional fluorescent dyes.

## 17.7 Sources of further information

Accounts of aspects of fluorescent dye chemistry and application technology feature in varying levels of detail in the range of general colour chemistry textbooks available (Christie, 2001; Gordon and Gregory, 1983; Hunger, 2003; Venkataraman, 1952–1974; Zollinger, 2003). More specific and detailed information on fluorescent dyes can be found in the textbook *Organic Luminescent Materials* (Krasovitskii and Bolotin, 1988), and in two review articles, one of which is general in nature (Christie, 1993) while a subsequent review focuses on the development of longer wavelength fluorescers (Mama, 1999). The excellent *Chromic Phenomena* (Bamfield and Hutchings, 2010) is worthy of special mention as it provides detailed current information not only on the chemistry of fluorescence but also on the technology of the modern devices which apply the phenomenon. There are numerous books and review articles devoted to specialist areas of fluorescent dye applications and these have been highlighted in the references given at appropriate points in this chapter. Perhaps surprisingly, the literature is less well-served

by accounts of the application of fluorescent dyes on textiles, and it is the author's hope that this chapter will provide a useful contribution towards addressing this gap.

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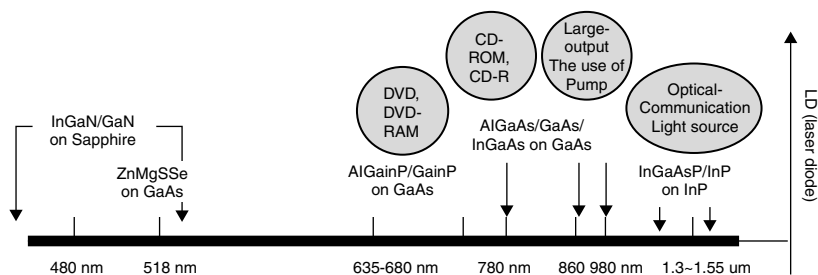
**Abstract:** This chapter provides a general overview of and information on near-infrared (NIR) absorbing dyes. NIR absorbing dyes have been considered in various recent high-tech applications such as laser optical recordings, laser printings, laser thermal writing displays, infrared photography and biological/medical applications. In optoelectronic application areas, especially, NIR absorbing dyes are being developed and new structural designs of the dye chromophore molecules are being studied. In this context, the chapter discusses general overviews and introductions for NIR absorbing dyes.

**Key words:** near-infrared, optoelectronic application, NIR absorbing dyes, high-tech dyes, functional materials.

## 18.1 Introduction

Near-infrared (NIR) absorbing dyes<sup>1-3</sup> have attracted significant interest for their uses in the development of functional materials for high-technology end uses. In optoelectronic application areas especially, NIR absorbing dyes are being developed and new structural designs of the dye chromophore molecules are being studied. These NIR dyes are very important key materials in the optoelectronics field and the display module area where they are used as extremely effective photo-receivers for the operating laser light source. After introducing gallium-arsenic (Ga/As), a semiconductor laser provides an emission wavelength which ranges from 780 to 830 nm. This is of great interest to those working in optoelectronic research particularly with optical recordings and laser printings.<sup>1</sup> Types of lasers and their application fields are illustrated in Fig. 18.1. The infrared wavelength ranges of the electromagnetic spectrum cover the area between the visible region and the microwave region.<sup>1,3-5</sup>

The infrared radiation spectrum is generally accepted and can be sub-classified into the near, medium and far infrared regions.<sup>4,6</sup> In this chapter,



18.1 Laser types and application fields with electromagnetic spectrum.

the dyes which absorb NIR regions, namely wavelengths from 700 to 2000 nm, are considered. The wavelengths from 750 to 1300 nm are particularly important in optoelectronic application. In this region, infrared radiation provides sufficient energy to the NIR dyes, which impart a  $\pi \rightarrow \pi^*$  transition of electrons within dye chromophore molecules. The importance of these NIR ranges is the reason that the gallium-aluminum-arsenide semiconductor lasers and the responding lasers absorbers, namely NIR absorbing dyes, are utilized in this region.<sup>3,4,7</sup>

Among the various types of dyes, cyanine type NIR absorbing dyes are well known and used in restricted applications in photochemistry. Following the dramatic increase in high-tech industries, new structural types of NIR absorbing dyes have been developed and introduced. Recently, the research focus on dye chemistry has changed greatly from traditional dyes and pigments for dye-houses to high-tech dyes for electro-optical industries.

NIR absorbing dyes have been considered in various recent high-tech applications such as laser optical recordings, laser printings, laser thermal writing displays, infrared photography and biological/medical applications.<sup>1-3,6</sup> Many research articles on NIR dyes have been published and the books on this subject are introduced by Fabian, Nakazumi, Matsuoka and Griffiths.<sup>1, 2,8,9</sup> This chapter will provide a general overview of and information on NIR absorbing dyes.

## 18.2 Properties of near-infrared (NIR) dyes

To absorb longer wavelengths such as those in the NIR region, NIR dye molecules are expected to meet the specific conditions in their structures.<sup>1-3,10,11</sup> The transition energy for excitation from ground state to excited-state needs to be lower, i.e. not more than  $150 \text{ kJ mol}^{-1}$ . Relatively easy approaches including calculated and designed structural synthesis can be used to achieve this.<sup>8,9</sup> Increasing the conjugation bond within the chromophore molecule is a good example for cyanine type dyes. The cyanine dyes have a highly uniform single-double bond alternation throughout their molecular structures

(Fig. 18.2) so a uniform bathochromic shift of the absorption band can be expected, with a vinylene shift order of 100 nm.<sup>3,8,9</sup>

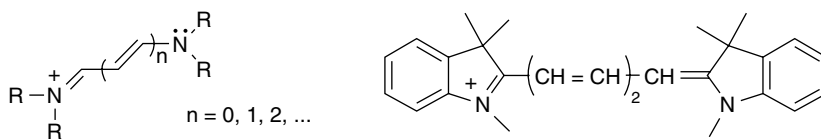
Introducing effective electron donating moiety in heterocycles is also a simple way to enhance NIR absorption (Fig. 18.3). This is a well established and reported empirical finding for the design of chromophore constitution. The maximum absorption wavelength can be shifted to the longer wavelength with increasing donating power of heterocyclic moiety.<sup>9</sup>

Similarly, a donor-acceptor electron transfer system<sup>8,12-14</sup> through dye chromophores could also be considered when designing NIR absorbing chromophores. This approach includes the following techniques:<sup>9,12-14</sup> increasing the length of conjugation between the donor and acceptor, enhancement of the electron donating-accepting power and modification within the conjugation linkage.<sup>1,3,9</sup> Structural replacement using nitrogen to carbon position<sup>2-4,8</sup> includes a useful bathochromic shift. Using this attempt, the absorption of dyes is observed in the NIR region. A further red shift can be achieved by increasing the electron donating strength of the donor group or of the donor heteroatom itself.

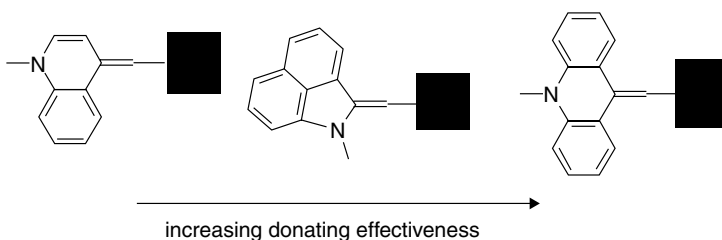
## 18.3 Types of NIR dyes

### 18.3.1 Phthalocyanine and naphthalocyanine dyes

It is well known that phthalocyanine chromophores<sup>1,2,4,15-20</sup> were first designed and synthesized as NIR absorbing dyes in 1928. After this introduction, phthalocyanine chromophores were structurally determined and recognized amongst the very important dye and pigment classes, especially those chromophores which showed the color blue.<sup>21-24</sup> Since their application



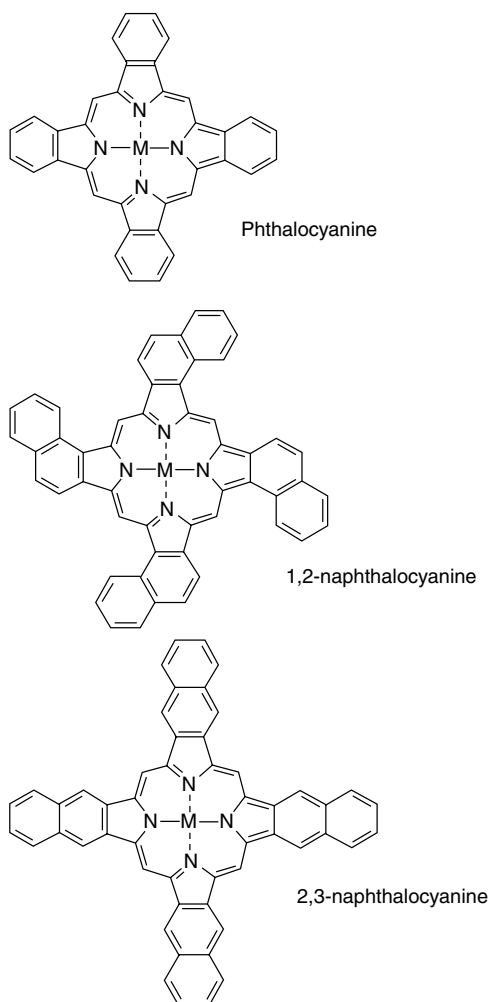
18.2 Example of cyanine dye structure.



18.3 Effectiveness increase with heterocyclic donor types.

in end uses as colorants, phthalocyanines have attracted great interest as a research subject.

During studies of the potential uses of NIR dyes, especially in the area of optical recording application,<sup>16,17</sup> phthalocyanines and naphthalocyanines<sup>1,17,25,26</sup> were utilized and typical examples are represented in Fig. 18.4.<sup>1,2</sup> The absorption wavelength of these dyes can be controlled between the ranges of 650 and 800 nm. Phthalocyanines containing metal ions generally absorb at a shorter wavelength, however phthalocyanine metal complexes with multiple substitution can provide an absorption wavelength shift to the NIR region.<sup>1,3,19</sup> Bathochromic shift can be also observed when



18.4 Basic structures of phthalocyanine and naphthalocyanine.<sup>1,3</sup>

changing from phthalocyanines to naphthalocyanines (Fig. 18.4), where the aimed wavelength can be controlled. For example, phthalocyanines consisting of 1,2-naphthalocyanines and 2,3-naphthalocyanines with an annular phenyl ring have shown a large bathochromic shift of the maximum absorption wavelength.<sup>1,2,10,26</sup> Applications to the optical properties of phthalocyanines and naphthalocyanines<sup>15,17</sup> such as laser disk memory, photography and recording media have been created in the areas of functional dyes. In order to achieve good solubility, the dyes have also had branched long-chain alkyl groups introduced into the benzene or naphthalene rings.<sup>3,9</sup>

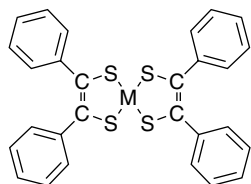
### 18.3.2 Metal-complex dyes

As colorant materials, metal-complex dyes<sup>1,4,9</sup> have been considered for use as mordant dyes. Complex dyes are, in general, insoluble or almost insoluble in water and organic solvents.<sup>27</sup> These dyes differ from conventional 1:1 and 1:2 metal-complex dyes for textile applications, which have one or more water-soluble sulfonic acid groups in their dye structures. For highly technical applications, some types of metal complexes, especially nickel complexes, have been used for dye laser, infrared absorbing film, antioxidant and singlet oxygen quenchers.<sup>28-30</sup> These dyes have also recently been successfully used with semiconductor laser diodes, which require NIR absorbing dyes and optical memory disk. Metal-complex dyes can be classified into three types (Fig. 18.5):<sup>1</sup> dithiolene metal complexes, phenylenediamine metal complexes and indoaniline-type metal complexes.

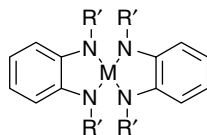
Metal-complex dyes have also been applied to the light absorbing media in laser optical memory devices. A cyanine dye layer film can reflect approximately 50% of NIR light, but the addition of metal complexes reduces this figure to approximately 15%.<sup>1,3</sup> The appropriate reading and writing properties cannot be achieved from these types of metal complexes. High reflectivity and acceptable absorption of NIR light can be obtained with indoaniline metal complexes and their films. The best known examples of metal-complex dyes which have the delocalized  $\pi$ -electron system are the nickel dithiolene complexes.  $\pi$ -electron's delocalized nature, where  $\pi$ -electron are delocalized over five membered rings, causes a long wavelength  $\pi \rightarrow \pi^*$  absorption band of high intensity.<sup>3,9,31,32</sup>

### 18.3.3 Polymethine dyes

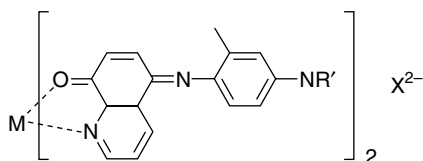
Methine dyes have been used for some time and cover a large wavelength region, in which the methine unit can provide a 10 nm absorbance shift with increasing unit numbers.<sup>4,11,17,33</sup> In other words, polymethine dyes show the well-known structure and their absorption ranges cover a wide range of



Dithiolene metal complex

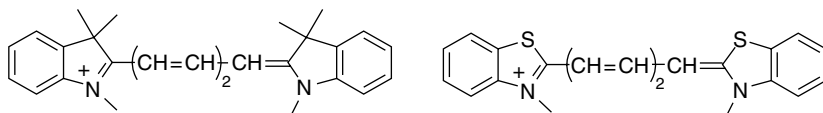


Phenylenediamine metal complex



Indoaniline metal complex

## 18.5 Examples of metal-complex dyes.



## 18.6 Examples of methine dyes.

wavelengths from 400 to 1300 nm.<sup>1,3,8,34</sup> Figure 18.6 shows the typical structure of polymethine dyes.

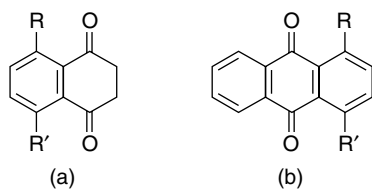
The dyes have cationic characteristics with positive charge heterocyclic nitrogen atoms at the ends of conjugated polymethine chains. The heterocyclic rings are generally placed at both ends of the dye structure.<sup>8,9</sup> The structural design of methine dyes commonly features heterocyclic moieties as the terminal donor groups. These terminal donor groups impart a more or less equal positive charge of chromophore molecules. The conjugating linkage is a polymethine unit, where the carbon atoms may be replaced by nitrogen atoms to give a bathochromic shift.<sup>12,13</sup> The  $\lambda_{\max}$  is strongly affected by the electronic characteristics of the heterocyclic moiety. In addition, the number of ethylene units in the conjugation linkage affects the  $\lambda_{\max}$ .<sup>1,3</sup> Generally at least  $n > 3$  of ethylene repeating units of the dyes are required to absorb in the NIR absorption region.

## 18.3.4 Quinone dyes

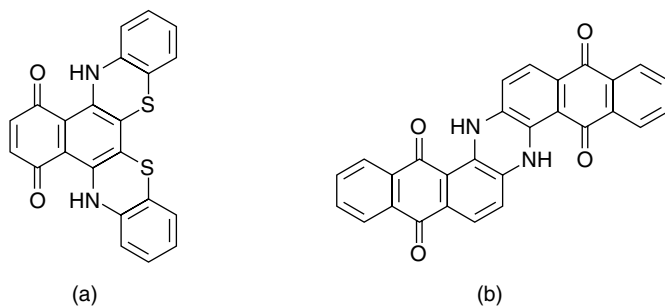
Dyes containing the quinone chromophore<sup>33</sup> have recently been used effectively in the dye colorant industry and a variety of ranges of quinone dyes have been marketed. Quinones are generally used as electron acceptors in dye design and synthesis. Donor and acceptor introduction into the quinone molecules causes wavelengths to change from a visible adsorption to an infrared one with an intramolecular charge-transfer (ICT) system.<sup>8,17</sup> Of the quinone chromophores, 1,4-naphthoquinone (a) and 9,10-anthraquinone (b) are the most common molecular units for the dyes (Fig. 18.7).

9,10-anthraquinones have been commercialized and used in traditional dye-houses. 1,4-naphthoquinones are not easy to synthesize and have unstable molecules. 1,4-naphthoquinones are, however, useful for dye development research using deep-colored dye chromophores. As mentioned previously, the introduction of donor substituents to the naphthoquinone and anthraquinone chromophores creates a wavelength shift to longer wavelength regions. These dyes can be utilized as optical recordings, liquid-crystal displays and dye diffusion thermal transfer systems due to their potential for producing deep color properties with a small molecular size.<sup>1,3,17</sup> Napthoquinone (a) and anthraquinone (b) analogues are shown in Fig. 18.8.

The use of optical recording media is the most popular research subject in the synthesis and characterization of infrared absorbing quinone dyes.<sup>35</sup>



18.7 Napthoquinone (a) and anthraquinone (b) structures.



18.8 Naptho- (a) and anthraquinone (b) analogues.



Many derivative dyes with the necessary properties for use in recording media applications, such as high sensitivity, low decomposition temperature and long lifetime, have been developed and their suitability confirmed.

### 18.3.5 Azo dyes

Azo dyes are one of the most widely used chromophores in dye chemistry. In general, however, they absorb in the visible wavelength region and are not suitable for NIR absorbing dyes. Their typical structural formula is shown in Fig. 18.9. This type of dye is used in many different dye classes in the textile dyeing industry and generally absorbs between 350 and 650 nm.<sup>1</sup>

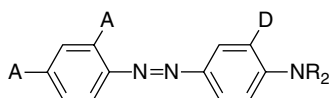
Using this azo dye, Griffiths *et al.*<sup>36</sup> introduced newly designed infrared absorbing azo dyes which had a strong ICT system in their molecular structure. These types of dyes generally absorb in the above 700 nm region. A thiazole heterocyclic ring was therefore positioned in place of the benzene ring which resulted in a large bathochromic shift to the infrared regions<sup>1</sup> (Fig. 18.10).

A further large bathochromic shift can be achieved by substituting the strong acceptor group, such as  $-\text{CN}$ , and increasing the  $\pi$ -conjugation system in the molecular structure.<sup>1</sup> It was Griffiths who described the dependence of the  $\lambda_{\text{max}}$  and molar absorption coefficient of the azo dyes on the donor-acceptor variations.<sup>1,36</sup>

## 18.4 Applications

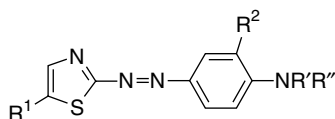
### 18.4.1 Optical recording

As the name implies, optical data recording<sup>1,3,4,9,35</sup> or optical data storage is a technique for storing and retrieving data using optical property



Acceptor =  $\text{NO}_2$ ,  $\text{CN}$   
Donor =  $\text{OH}$ ,  $\text{NHR}$ ,  $\text{NR}_2$

18.9 Basic structure of azo dyes.



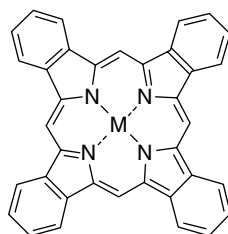
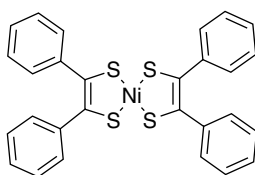
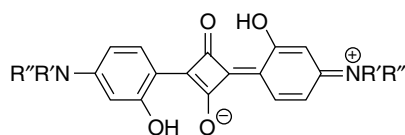
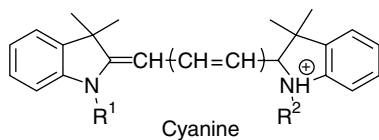
18.10 Example of modified azo dye structure for NIR absorption.

applications.<sup>37,38</sup> Disks or tapes were widely used for most data storage but in order to increase the amount of data per unit area, a new type of recording method using optical properties was developed. Optical data recording is a similar application to conventional magnetic data storage. The data recording technique involves a semiconductor laser writing the data on the optical disk surface and the same weak laser is used to read it.<sup>3,9</sup> The optical disk has a thin (1.0–0.1  $\mu\text{m}$ ) uniform film of NIR absorbing dyes on a polymethylmethacrylate substrate. For this technique, lasers with an 780–830 nm emission wavelength were used. The laser radiation of 10 mw hits the disk surface and the resulting hole is formed by the coated infrared absorbing dye.<sup>6,11</sup> These formed pits record the data. After this writing step, a lower power laser with the same emission wavelength is used to read the recorded data. At this stage, the laser radiation energy is insufficient to cause melting of the original pit which would erase the previously recorded/written data. In this way, a detector records the amount of laser reflected from the disk.<sup>1,3,5,9</sup>

As a consequence of these properties various classes of infrared absorbing dyes<sup>39–41</sup> have become increasingly popular for use in optical data recording<sup>5</sup> including cyanines, squaryliums, nickel dithiolenes and phthalocyanines<sup>3,4,9</sup> (Fig. 18.11). In studies of optical disk application cyanines showed high absorption coefficients, but their durability was too low whereas squaryliums had better durability, but lower absorption coefficients. Nickel dithiolenes showed moderate properties for both absorption coefficients and durability but high absorption coefficients and a good durability were achieved by phthalocyanines.

#### 18.4.2 Heat-absorbing NIR dyes

The energy distributions of sunlight cover 50% of the visible range and 50% of the infrared range. This infrared light is commonly considered to be thermal light and is an equivalent of heat energy.<sup>10</sup> Thus, to absorb or to block the energy of infrared heat, broad ranges from 750 to 2000 nm should be covered.<sup>9</sup> Phthalocyanine dye derivatives are the best option for this since they absorb around 880 nm of infrared light and, as a result, block the heat energy.<sup>10</sup> In other cases, the dyes used can change the energy distribution of the light. After absorbing the light at the maximum wavelength they then emit it at another shifted wavelength using their fluorescent functions. Some examples are car windscreens, windows of buildings and agricultural films. To meet this demand a high durability is required of the light, especially when used in long and severe exposed conditions.<sup>11</sup> NIR dyes need to be able to efficiently absorb infrared light to be used as shielding materials from the heat. These NIR dyes are generally used with dispersed states in a polymer matrix such as polymethylmethacrylate, polycarbonate,



#### 18.11 Dye examples of the use of optical disks.

polyethyleneterephthalate and so on,<sup>3,4</sup> in which capacity they are used as shielding materials as mentioned in the previous examples.

Of the many dye chromophores which absorb infrared light, phthalocyanines are considered to be the most suitable dye materials due to their quickness to light.<sup>5,9</sup>

#### 18.4.3 Laser printers

A semiconductor diode laser is currently used in laser printers as the light source. It emits NIR light at around 800 nm wavelengths. To respond to this

NIR light, photoconductive materials sensitive to an NIR wavelength such as infrared absorbing dyes are used as photo-receivers.<sup>3</sup>

An organic photoconductor (OPC)<sup>1,10</sup> is an important key material for the laser printing device. This OPC is divided into two consisting layer materials, the charge generation material (CGM) and the charge transportation material (CTM).<sup>3</sup> There are many dyes which can be used in CGM and CTM layers. Bisazo dye, squarylium dye, phthalocyanine dye and trisazo dye are just some of the examples. Azulanium dye and naphthocyanine dye are also used for the OPC, which absorbs NIR light.<sup>8,11</sup>

#### 18.4.4 Chemosensors

Optical chemosensors using NIR dyes, such as indoaniline, phenyliminoquinoline, vinylene carbenium, squaraine, cyanine and nitroso type, have been the focus of considerable research efforts and various chemosensing systems have been introduced in recent years.<sup>42-44</sup> The sensing element/reagent is an important key component in the chemosensing system and generally a dye is used. Most of the research on optical chemosensors has been conducted in the visible region, but a minimum optical attenuation in the NIR region is necessary. For this reason, NIR absorbing phthalocyanine dyes have been used in a variety of high-tech applications.<sup>1,3,4,42</sup> Phthalocyanine dyes were very stable when used in thermal, chemical and physical applications and also provided very narrow and intense optical band properties. A great deal of information on their chemistry has been reported.<sup>5,8,11,17</sup> The phthalocyanine molecules have strongly delocalized  $\pi$ -electrons, where  $\pi \rightarrow \pi^*$  transitions result in strong absorption bands in the visible region. The addition of benzene rings and electron donating substituents, however, shifts the absorption bands from the visible to the NIR region by increasing the length of  $\pi$  electron conjugation and electronic delocalization.<sup>9</sup> Other types of dyes such as quinoline, carbenium and squaraine dye have also proved useful in chemosensing applications.<sup>17</sup> Simon *et al.*<sup>45</sup> reported ammonia sensing findings using these three types of NIR dyes. These NIR absorbing dyes are important, because the absorption bands of other materials are minimal in this region of 700–900 nm and do not overlap with the absorbance of NIR absorbing chromophore. Recently, attempts to prepare acid-base indicators for absorbing in the NIR region have been made to develop chemosensors.<sup>46-54</sup> Metal complexes, squaraine dyes and methine dyes have been considered for use in this endeavour, especially for ammonia sensing in both gas and liquid phases.<sup>45,55</sup>

### 18.5 Future trends

Creating a camouflage effect in the non-visible range, NIR region 700–1300 nm, is of particular importance especially for military applications.

Camouflage materials, therefore, need to be coated or dyed with dyes which have NIR reflectance properties similar to those of the background material. To avoid the detection of an object, resolution reduction is required between the object and its surroundings.<sup>56</sup> In this way NIR dye materials can be utilized to protect equipment and lives. The considered NIR region with respect to camouflage is 650–900 nm.

NIR dyes can also prove useful in medical applications. Light in NIR ranges (700–900 nm) effectively traverses tissue due to the low absorption by water and hemoglobin in this spectrum range. NIR dyes can therefore be applied in optical-based molecular imaging where fluorescent proteins or fluorescently labeled antibodies are used. Any fluorescent dyes used for optical imaging need to meet the following requirements in order to be acceptable for *in vivo* diagnostic imaging:<sup>57–59</sup>

1. Excitation and emission should be in the 650–950 nm NIR region
2. High extinction coefficient
3. Strong fluorescence intensity
4. Durability for photo-fading
5. No light-induced sensitizing effect
6. Hydrophilic.

Given these criteria cyanine dyes would be the best option due to their high extinction coefficients and their absorption and emission region from visible to NIR spectrum.<sup>57–65</sup> There is a growing need in medical imaging research to monitor and determine target tissue and disease processes. Current research focuses on the development of new NIR fluorescent dyes and monitors various biological examples with these dyes being used as fluorescent labeling reagents.<sup>66</sup> NIR fluorescent dyes are highly conjugated molecular structures and possess a lower energy gap between the ground and the excited states. Cyanine dyes, squaraine dyes and thiazine/oxazine dyes are commonly used as the NIR fluorescent dyes<sup>67–73</sup> but a new type of aza-dipyrromethene boron difluoride dye has been reported,<sup>74</sup> which provides a high chemical stability and photostability function. Additionally, porphyrin and metal-complexed phthalocyanine dyes have also shown absorption and emission properties in both the visible and NIR regions.<sup>75–78</sup>

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**Abstract:** Azoic colours are mostly applied to cellulosic materials. This chapter discusses the principles of azoic colour application, its various steps and chemistry, advantages, disadvantages and environmental effects. This chapter also discusses the fastness properties of azoic colours and how to tackle rubbing fastness problems associated with these colourants.

**Key words:** azoic, bases, diazotisation, dyeing, naphthols, toxicity.

## 19.1 Introduction

The azo compound class accounts for 60–70% of all dyes. As one might expect, they all contain an azo group,  $-N=N-$ , which links two  $sp^2$  hybridised carbon atoms. Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two (disazo), three (trisazo) or more.

While azo dyes are ready-made dyes, azoic colours are formed inside the textile materials, *in situ*, by reaction of two colourless or lightly coloured compounds called naphthols, or C.I. Azoic Coupling Component (ACC) and fast bases, or C.I. Azoic Diazo Components (Ghosh, 2004). Azoic components are defined in the *Colour Index* as those used to produce ‘insoluble azo dyes *in situ*’ usually on a textile substrate.

The azoic colours are produced *in situ* on the textile materials in four stages. Firstly, the naphthols which are insoluble in water are converted to water-soluble species by a process called dissolution of naphthol. Secondly, the naphthols are applied on textile materials by a process called *naphtholation* as they have some affinity for the cellulosic materials. Thirdly, the base is diazotised, by a reaction called *diazotisation* and finally the naphtholated material is treated with the soluble diazotised base, which forms an intense colour in the substrate. The final step is known as coupling or development. The first synthetic dyes produced by diazotisation and coupling in two distinct steps were performed by Caro and Witt in 1875 at BASF (Zollinger, 2003).

## 19.2 Advantages and disadvantages of azoic dyeing

The major advantages of azoic colours are (Chavan, 1999; Roy Choudhury, 2006; Shore, 1995):

1. Materials can be dyed in various physical forms of textile materials in various machines or even in short batches using domestic utensils in the absence of machines.
2. Dark blue, black, orange, red and bordeaux shades can be obtained economically.
3. Dyeings have excellent reproducibility.
4. Commercial economic viability.
5. Most combinations are dischargeable.
6. The fastness properties, in general, are good.

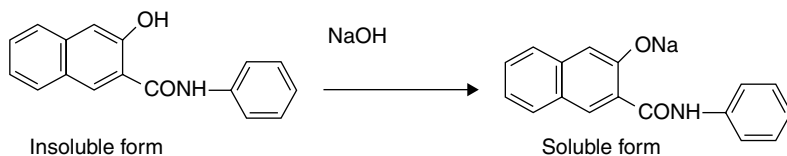
There are certain limitations of azoic colouration of textiles. They are as follows:

1. The application procedure is complicated and time-consuming.
2. A number of chemicals are to be used and stored. Difficulties of handling the component chemicals under typical chemical process house conditions, especially the diazotisation of aromatic amines fast bases.
3. The fastness to rubbing of azoic dyed material has always been a problem. Efficient removal of excess naphthol from the surface of treated material, high substantivity of the coupling component and thorough soaping after development are essential to achieve good rubbing fastness.
4. Limited shades available.
5. Compound shades as produced with other dye classes by mixing three/four dyes is difficult with azoic dyes since there would be cross coupling between various naphthols and diazonium salt and the mixed shades are unpredictable and non-reproducible.
6. The final shade is only visible only after coupling stage. Hence, any unevenness, caused during naphtholation, may be undetected and is only visible after coupling when shade correction is difficult.

## 19.3 Chemistry of azoic dyeing

### 19.3.1 Naphthols

The naphthols are insoluble in water. They are phenols, soluble in alkaline solution and substantive to cotton, particularly in the presence of salt. In the presence of strong alkali they are converted to the corresponding naphtholate ions and are water soluble (Fig. 19.1). The naphtholate ions are always



19.1 Solubilisation of naphthol (conversion of naphthol to naphtholate).

coplanar and preferably have elongated molecular structures. These relatively small molecules are of low to moderate substantivity for cotton. The naphthols may be classified into four groups depending on their affinity for cotton (Shenai, 1993).

- (a) Low substantivity naphthols: Naphthol AS, Naphthol ASD, Naphthol AS-OL, Naphthol AS-IRG, Naphthol AS-PH, etc.
- (b) Medium substantivity naphthols: Naphthol AS-BG, Naphthol AS-LT Naphthol AS-RL, etc.
- (c) High substantivity naphthols: Naphthol AS-BS, Naphthol AS-SW Naphthol AS-BI, Naphthol AS-BO, etc.
- (d) Very high substantivity naphthols: Naphthol AS-BT, Naphthol AS-S Naphthol AS-BT, Naphthol AS-BR, etc.

In general, the higher the substantivity the better the rubbing fastness since less azo pigment forms on the fibre surfaces. The substantivity increases with increase in the molecular size of the naphtholate ion, but the diffusion rate in the fibres and solubility in dilute aqueous alkali decrease. Addition of salt promotes better exhaustion of the bath, more being needed for naphthols of lower substantivity. For the dissolution of naphthols usually caustic soda solution of 72°TW, i.e. 38°Be, is used. The first ACC, which was employed in the commercial synthesis of azoic colour, was the 2-hydroxy-naphthalene, i.e. Beta-naphthol. The same was later replaced by more substantive aryl-amides of 2-hydroxy-3-naphthoic acid discovered in 1911 in Germany. This product is known today as Naphthol AS. With different substitutions on the basic structure, several other substantive naphthols were subsequently developed in the following years which were named as members of the Naphthol AS series (Table 19.1).

A correlation between the chemical structures of ACCs and their affinity for cotton has been attempted. The theoretically computed correlation equations of the practical affinity with the van der Waals surface, the molecular volume and the hydrophobicity are reported in the literature (Dăescu and Hădă Ruga, 1999).

Though reversing the position of amino groups in the conventional AS series of naphthols was found to enhance the brightness of the developed

Table 19.1 Examples of some naphthols (ACC)

Naphthol	Substantivity	Structure	C.I. constn. no.	ACC
$\beta$ -Naphthol	—		—	—
Naphthol AS	Low		37505	2
Naphthol ASD	Low		37520	18
Naphthol AS-BG	Medium		—	19
Naphthol AS-OL	Low		37530	20
Naphthol AS-PH	Low		37558	14
Naphthol AS-SW	Higher		37565	7
Naphthol AS-BO	Higher		37560	4

shade, significant advantages over conventional products were not achieved (Hall *et al.*, 1980).

### 19.3.2 Bases

For *in situ* synthesis of azoic pigment on the textile material, the naphtholated material has to be developed in a bath containing a suitably prepared second component, usually referred to as a Fast Base. These are available as the free amine base or as amine salts such as hydrochloride. Many of the amines used are simple substituted aniline derivatives. Some of these components are free bases ( $R-NH_2$ ), while others are hydrochlorides of

the bases ( $R-NH_2.HCl$ ) and a few of them are hydrogen sulphates. The so-called Fast Colour Bases require diazotisation for coupling with the naphthol. This usually involves reaction of the primary aromatic amine in acidic solution or dispersion with sodium nitrite, at or below room temperature. Diazotisation of a primary aromatic amine is often difficult and solutions of diazonium ions are inherently unstable. They undergo decomposition even at low temperature and particularly on exposure to light. Storing prepared diazonium ion solutions is not usually possible.

## 19.4 Colours obtainable using azoic components

Table 19.2 shows some examples of the colour developed by various combinations of naphthols and fast bases. The first step in selecting the most suitable naphthol (coupling component) and fast base (diazo component) for a particular purpose is to decide which of the available naphthols, after dissolution, give anions with suitable substantivity for application by the desired method. The second step is to decide which of these naphthols can be used in conjunction with the available diazo components to produce the colour closest to the desired shade and depth (Aspland, 1997).

## 19.5 Methods for dissolution of naphthol

As discussed in Section 19.3.1 the naphthols are not soluble in water but their sodium salts (naphtholates) are water soluble. The first step for the production of azoic colour on textile materials is, therefore, the dissolution of naphthols.

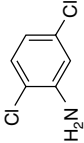
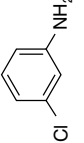
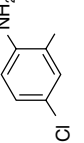
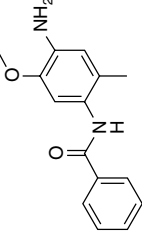
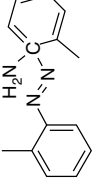
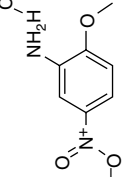
### 19.5.1 Hot dissolution method

Naphthol is pasted with a wetting agent such as Turkey Red Oil (TRO) and hot, soft water is poured over the naphthol paste. After a short boil, hot caustic soda solution is added and the mixture is heated until a clear solution of naphthol is formed, which is ready for application (Trotman E R, 1994). Some naphthols, especially those with poor substantivity and generally difficult to dissolve, are marketed in a special form that dissolves easily and quickly.

### 19.5.2 Cold dissolution method

In this technique of dissolution, naphthol is pasted with industrial alcohol and warm water and then converted to the naphtholate by adding caustic

Table 19.2 Examples of some bases and their combination colours with various naphthols

Bases	Structure	Coupling rate	Group	Colour produced with various naphthols							
				AS	AS-G	AS-SW	AS-D	AS-BR	AS-BG		
Scarlet GG		Rapid	Group 1	Bright yellowish red	Bright yellow	Bright yellowish red	Bright Orange	Reddish brown	Brown		
Orange GC		Medium	Group 1	Bright red	Bright yellow	Bright yellowish red	Yellowish red	Reddish brown	Reddish orange		
RedTR		Medium	Group 2	Bright red	Bright yellow	Bright red	Yellowish red	Reddish brown	Dull red		
Violet B		Medium	Group 3	Bright blues violet	Reddish yellow	Dull reddish violet	Dull violet	Dull bordeaux	Bluish red		
Garnet GBC		Slow	Group 1	Dull bordeaux	Yellowish orange	Dull bordeaux	Dull reddish violet	—	Dull bordeaux		
Scarlet RC		Medium	Group 1	Bright red	Yellow	Bright red	Bright red	Reddish orange	Bright red		

soda. Alternatively, a mixture of water, caustic soda and methanol can be poured over naphthol which is brought into solution by stirring.

The cold dissolution technique is used for batch-wise application of naphthol, where treatment is carried out at room temperature. The hot dissolving method is suitable for pad application near boil. More concentrated solutions of naphthols can be prepared by the cold dissolving method, but this is more expensive because of the requirements of methanol.

## 19.6 Naphtholation and dyeing of cotton

The treatment of textile materials with naphthol solution is called naphtholation. The method of azoic dyeing discussed in this chapter is based on cotton unless specifically stated. When cotton textiles come into contact with naphthol solution, exhaustion begins at a rate depending on the substantivity of the fibre for the naphthol. Application of naphthol may be carried out either by exhaust technique or by continuous method using padding mangle. Naphthol is mostly applied to either yarn or fabric. Yarn is either dyed in a package dyeing machine in package form or in hank form in an open beck liquor circulating type machine. For smaller lots and heavy fabrics a jigger is used for dyeing.

High substantivity naphthols are usually preferred for batch-wise application whereas naphthols of low substantivity are used for continuous applications. The exhaustion of low or medium substantivity may be improved by addition of electrolyte in batch applications. The affinity of most of the naphthols decreases with increase in the temperature of application. However, this is not the case with Naphthol AS-BR, Naphthol AS-LR, etc. (Shenai, 1993). Since the exhaustion of naphthol decreases with increase in temperature, batch-wise treatments are normally carried out at 30–40°C. If improved wetting or penetration is required the temperature may be increased to 50°C. However, this temperature should not be exceeded if formaldehyde is added to naphthol. It is essential to prepare the naphthol solution just before use as the stability of naphthol solution and the naphtholated material is limited. A 20–30 min treatment is generally the required treatment time. The effects of various types of alkali on the rate of absorption of different naphthols are discussed in the literature (Hückel, 1958).

### 19.6.1 Strength of azoic dyeings

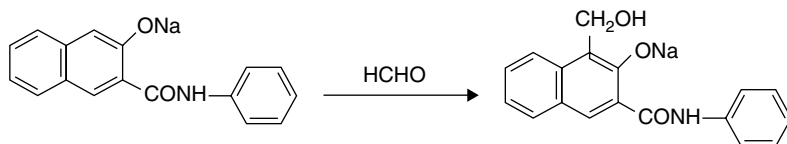
The depth of dyeing obtained with azoic colours is controlled by the amount of naphthol applied. Dyeings are defined by the quantity of naphthol fixed on cotton and designated as g/kg naphthol. The depth of dyeing in batch application depends on the concentration of naphthol solution, liquor ratio,



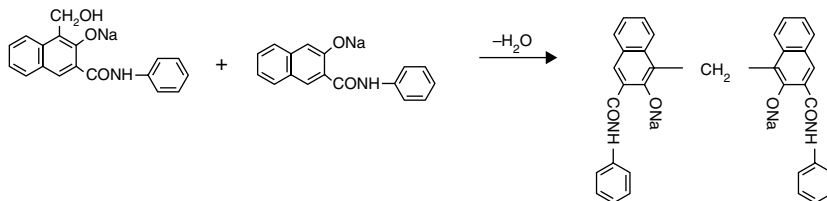
the form of textile to be dyed and the concentration of electrolyte added, if any. Manufacturers of naphthol colours supply graphs and tables which indicate the concentration of naphthol for batch-wise application at a specified liquor ratio to obtain the dyeing of the depth desired (expressed in terms of naphthol/kg of substrate). For pad application the applied concentration (g/L) can be calculated from the desired depth (g/kg) from the padding liquor (Chavan, 1999). It is advisable to refer to the manufacturer's literature for reliable guidance.

### 19.6.2 Ingredients of naphtholating bath

Addition of wetting agent in the naphtholating bath helps in rapid wetting of material. TRO serves this purpose. However, alkaline earth metals present in hard water react with TRO to form insoluble soap. Therefore hard water should be avoided in the naphtholating bath. If soft water is not available water softening agents such as polyelectrolyte, ethylenediaminetetraacetic acid (EDTA), etc., may be used. The amount of sodium hydroxide necessary in dyeing is greater than the theoretical amount required to convert the naphthol into naphtholate. A minimum concentration of sodium hydroxide in the naphtholating bath is necessary which depends on the depth of the shade. The literature supplied by the manufacturer should be referred to for this purpose. The sodium salt of naphthol tends to hydrolyse, in solution, with the formation of free naphthols. When naphthol treated material is exposed to air, the acidic fumes or carbon dioxide present in air convert the naphtholate into insoluble naphthol. Normally free naphthols do not couple with diazonium salts. The resistance of naphthol to atmospheric carbon dioxide can be increased by the addition of formaldehyde to the naphtholate bath. Due to the introduction of methylol group (Fig. 19.2) in the structure of the naphtholate its resistance towards hydrolysis is enhanced. The material after treatment with formaldehyde should not be exposed to high temperature as these methylol compounds are converted into methylene compounds which blocks the coupling position leading to loss of coupling power of the naphtholate (Fig. 19.3). Addition of formaldehyde to the naphtholate solution should be conducted at room temperature to avoid formation of methylene bridge. A number of naphthols such as Naphthol AS-OL, AS-BS, AS-LB, AS-ITR, AS-PH, etc., have good stability even in the absence of formaldehyde. Some other naphthols such as Naphthol AS-SW, AS-G, AS-LG lose their coupling power when formaldehyde is added. Hence, the formaldehyde should not be added in these cases. The exhaustion of naphthols, particularly those of low to moderate substantivity, can be increased by the addition of common or Glauber's salt. Electrolyte is recommended to be added in the application of long liquors. The amount of electrolyte depends



19.2 Treatment of naphthol with formaldehyde to form methylo compound.



19.3 Formation of methylene bridge at high temperature.

on the individual naphthol and ranges between 10 and 40 g/L for common salt. The electrolyte is always added in the dissolved form. The quality of salt is very important. It should be free from other metallic salts especially alkaline earth metal salts. The vapour pressure, latent heat of sublimation and associated entropy changes of various derivatives of Naphthol AS have been determined by transpiration method and reported by Nishida *et al.* (1983). Dyeing of cellulosic fabric with reactive dyes in presence of an ACC is described by Ethirajan (1994).

## 19.7 Intermediate treatments

The naphtholated material contains both properly absorbed as well as superficially held naphthol solution on the surface of the textiles. Both these portions of the naphthols react with the diazonium chloride of the developing bath resulting in the formation of the azoic pigment. The pigment formed by substantively held naphthol is firmly bound in the textile material while that formed by the unfixed/superficially held naphthol is loosely held on the surface of the textile material. These loosely held pigments if not removed efficiently will adversely affect the rubbing fastness. Azoic dyed materials with poor rubbing fastness is a common problem in the industry. There are three ways to tackle this problem: (a) removal of excess/unabsorbed naphthols from the naphtholated material by suitable techniques such as rinsing, suction, wringing, mangling or hydroextraction; (b) selecting naphthols of high substantivity; (c) thorough boiling treatment with a solution containing soap or any good synthetic detergent and soda ash. To minimise the poor rubbing fastness defect the naphtholated material is subjected to removal of excess liquor by a suitable technique. Hydroextraction is the most efficient

method for removing unabsorbed liquid. Optimum conditions can reduce the liquid content to 40% by weight of cotton. Employment of methods such as suction, squeezing or wringing depend on the type of material, i.e. loose stock, yarn in hanks, wound packages for fabric.

The final concentration of naphthol on the fabric naphtholated on jigger or yarn treated in package dyeing machines may be reduced by rinsing. It comprises treatment with 10–15 g/L common salt and 1–2 mL/L caustic soda (32.5%) for 5–10 min. 10–30 g/L common salt is used with highly substantive naphthols and 30–50 g/L with naphthol of low to moderate substantivity.

In continuous dyeing excess liquor is removed by drying the fabric. Care must be taken to avoid sudden drying to prevent uneven absorption of naphthol due to migration leading to uneven drying. Therefore, predryers are sometimes used. Predryers that can reduce the moisture level rapidly to 30–35% are helpful. The drying can be performed in hot flue, float dryer, stenter or drying cylinders. But, regardless of the type of dryers used, the amount of moisture left on the goods should be in the range 9–12% (14% for viscose). The most appropriate temperature for final drying is between 90 and 110°C. This is controlled by the temperature and speed of drying. Careful drying after naphthol application leads to dyeing of high fastness on development (Wiltshire, 1954).

## 19.8 Development

After naphtholation and subsequent treatments such as hydroextraction, rinsing or drying the material passes into the development bath which contains a dilute solution of a diazonium salt. This is produced either by diazotisation of an aromatic amine, a so-called fast colour base or by dissolving stabilised diazo fast colour salt which is commercially available in solid form.

### 19.8.1 Diazotisation of fast bases

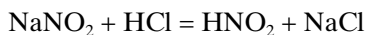
The process of conversion of aromatic amines (in the present case fast bases) into its reactive form, diazonium compound, is called diazotisation (Hodgson and Norris, 1949). This reaction is a valuable tool not only in the application of azoic colours, but also in the synthesis of a large number of dyestuffs having azo groups.

The reaction involves two steps (Ridd, 1959):

1. Conversion of the free base into its water-soluble salt, usually hydrochloride. This is carried out by treatment with concentrated hydrochloric acid and by heating or boiling, if necessary.



2. The reaction of the hydrochloride of the base with nitrous acid is usually done at low temperature (ideally 0–5°C). Generally a temperature range of 8–12°C is economical and is achieved by adding ice into the diazotising bath. This is carried out by adding sodium nitrite into a solution of the hydrochloride of the base in presence of excess hydrochloric acid.

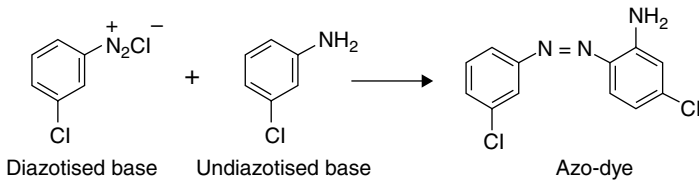


Formation of a clear final solution and the absence of froth indicate successful diazotisation. The diazonium salt is unstable even at room temperature in that it reacts with water and is decomposed. This decomposition is accelerated by heat and light. Contact with metal surfaces also encourages decomposition of the salts so the diazotisation reaction should not be carried out in metal containers.

There are two methods available for diazotisation, namely direct and indirect methods. In the former method the base is pasted with a little water and the required amount of concentrated hydrochloric acid. The mixture may be required to be heated for complete dissolution of the base. When the base is completely dissolved, the solution is cooled by adding crushed ice to the solution. When required temperature is attained, the recommended quantity of sodium nitrite pre-dissolved in a small quantity of water is slowly added with stirring. The mixture is left for some time for completion of diazotisation reaction; typically it takes 20–30 min for complete reaction to occur. In the indirect method the base is pasted with a small quantity of water. Solid sodium nitrite is then thoroughly incorporated until dissolved. In another bath, hydrochloric acid mixed with crushed ice is prepared. The mixture of the base and nitrite is then slowly added to the second solution with constant stirring and diazotisation takes place.

The bases such as Fast Orange GC base, Fast Yellow GC base, Fast Scarlet TR base, Fast Red KB base, Fast Red RC base, etc., are marketed in the form of their hydrochlorides. In these cases, since they are already soluble in water, they may be dissolved in a large volume of water. Hydrochloric acid should be added to this solution to avoid hydrolysis of the salt.

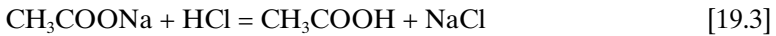
Both hydrochloric acid and sodium nitrite/nitrous acid should be present in sufficient quantity during diazotisation. If either of these compounds is found to be deficient, suitable additions should be made; otherwise the entire base is not diazotised. If the system lacks in hydrochloric acid, the diazotised base reacts with undiazotised base, forming an azo dye (Fig. 19.4). The resultant dye cannot react with naphthol to form azoic pigment during the development stage which results in the loss of a part of the base. The dye formed due to the coupling of diazotised and undiazotised base may have a



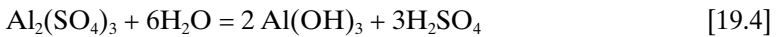
19.4 Coupling of diazotised base with undiazotised one.

colour different from the intended one thus the intended shade will be discoloured due to this dye. The presence of hydrochloric acid is confirmed by Congo Red paper, which turns blue when dipped in the solution. A starch-iodide paper turns blue, if nitrous acid is in excess.

At the end of diazotisation, the solution contains a large amount of hydrochloric acid. For proper coupling subsequently, the pH is to be raised to 5.0–6.0 by adding sodium acetate



The naphtholated material even after removal of excess naphthols contains a high concentration of alkali and when such material is introduced into the developing bath, the pH of the latter increases which in turn adversely affects the rate of coupling reaction. In order to neutralise this alkali, an alkali-binding agent, namely alum or acetic acid, is added to the diazotised solution. Alum releases sulphuric acid in the bath as follows:



However, the addition of alum may alter the shade of certain azoic combinations. Hence, acetic acid is preferred. Sodium acetate and acetic acid act as buffers and maintain the pH at the required value.

### 19.8.2 Stabilisation of diazonium salts

Since the application of azoic colours to textile materials is essentially a two-step process and since it involves the carrying out of time-consuming diazotisation reaction by the finisher in the process house, there was a need to simplify the operation and this could be done only by stabilising the diazotised bases, so that the dyer or the printer was spared the trouble of diazotising the bases. This has been made possible by various approaches and now ACCs along with the stabilised diazo components in a single mixture are available without the need for prerequisite coupling. These mixtures are applied by printing using a one-step process.

Various methods of stabilisation have been developed to produce fast colour salt (consisting of diazotised and stabilised primary aromatic amines) which can be directly dissolved in water to obtain the diazonium chloride ready to be coupled with the coupling components.

Stabilisation methods for diazonium chloride can be broadly classified into two categories, namely active stabilisation and passive stabilisation. Active stabilised products, when dissolved in water or alcohol, are readily converted into diazonium salts, which couple immediately when they come into contact with the azoic coupling compounds. Passive stabilised products do not form the diazonium salt when dissolved in water and as such they remain inert when mixed with the azoic coupling compound. Passive stabilised products therefore can be mixed with ACCs without coupling taking place. Activation of passive stabilised products can be carried out either by acid treatment or by steaming.

#### *Active stabilised diazo compounds*

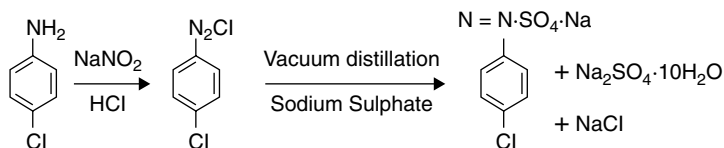
These are commercially called fast salts. As a general rule solutions are prepared by pouring over the fast colour salt five times its weight of lukewarm (25–30°C) water containing a non-ionic dispersing agent and stirring until dissolved. Acetic acid or formic acid may be required with some fast colour salts. Most of the fast colour salts contain an alkali-binding agent so that in most cases no further addition is required. The solution of the fast colour salt should not be allowed to stand too long. The various ways of forming stabilised diazonium salt are as follows.

- Stabilisation by conversion into sulphates or chlorides of the diazonium salt:

In this case the acidic solution of the diazonium salt is evaporated under vacuum at 45°C which, when treated with anhydrous sodium sulphate, is converted to a solid of the sulphate salt of the diazo compound (Fig. 19.5)



- Stabilisation by formation of complex salts of diazonium compounds:  
The basicity of the diazonium compound is exploited to form double salts of metals such as chlorides or other halides of metals. Tin, mercury,



19.5 Stabilisation of diazonium salt by sulphate formation.

zinc, iron cadmium and antimony salts are capable of forming double salts. Zinc chloride double salts with diazonium salts are the most important among the various methods of stabilisation.



### Passive stabilisation

The passive stabilised product can be mixed in the dry state with a naphthol without the danger of premature formation of the azoic pigment. These products are used by printers. The passive stabilised diazo components may be classified as follows:

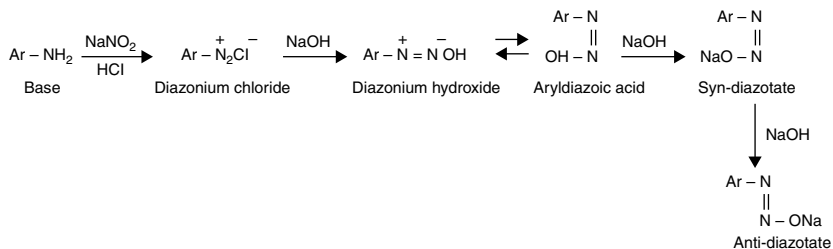
1. Antidiazotates
2. Diazoamino compounds
3. Aminosulphonic acids
4. Diazosulphonates

- Antidiazotates

In this case the aromatic diazonium chloride is treated with a strong solution of caustic soda (106° TW) which converts it into an unstable diazonium hydroxide. The later isomerises to a diazoic acid. The acid is then isolated in the form of its sodium salt (diazotate) by treatment with sodium hydroxide. The aromatic diazotate thus formed exists in two forms: syn-diazotate and anti-diazotate. The syn-form is the reactive form whereas the anti-form is very stable and can be obtained even in solid form. The reactions involved in this conversion are shown in Fig. 19.6. The anti-form does not couple with a naphthol and thus can be kept along with a naphthol in a single packet. This combination is known as Rapid Fast. The mixture on acidification converts the anti-form into the active syn-form of the diazotate which then immediately couples with the naphthol.

- Diazoamino compounds

Diazoamino compounds are formed by treatment of the diazonium chloride with a suitable amino compound, called 'stabiliser'



19.6 Stabilisation by anti-diazotate formation.

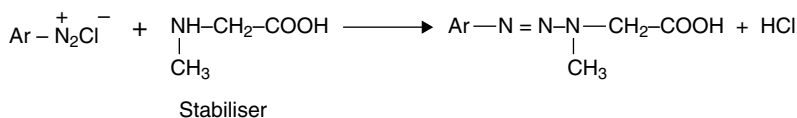
(Fig. 19.7). This is the most commonly used product among all the stabilised azoics. The diazonium compound has no coupling power and is stable in neutral or alkaline solution. The mixture of diazoni-amino compound and a naphthol is marketed under many trade names; one such name is Rapidogen dyes. The diazonium salts, stabilised by reacting with an amino compound are also called tri-azenes. The mixture is dissolved in an aqueous alkaline solution. On acidification, the diazoamino compound is converted into an active diazonium salt, which immediately couples with the naphthols present and forms the azoic pigment.

- Aminosulphonic acids

In this method of passive stabilisation, the base is first treated with chloro- sulphonic acid to obtain the aryl sulphonic acid. The acid is mixed with sodium nitrate, and a suitable ACC, when coupling does not take place. When the mixture is acidified, the diazonium salt is formed, which then couples with the naphthol present and forms the azoic pigment.

- Diazosulphonates

Diazo compounds when reacted with alkali metal sulphites in neutral solution form a solid salt-like product known as diazosulphites, diazosulphonic acids or diazosulphonates. These products are soluble in water and produce an inactive diazo compound, which requires careful oxidation (e.g. with sodium chromate) under neutral conditions to activate them. The passive stabilised diazo compound may be mixed with a suitable naphthol. Such mixtures are marketed as Rapidazole dyes. The mixture is applied by dissolving the dye in an aqueous solution of sodium hydroxide containing sodium chromate, which is then printed onto the textile substrate in the usual manner. When the prints are exposed to neutral steam for about 10 min, the inactive diazosulphonate is oxidised to the active diazosulphite, which then combines with the ACC present in the mixture. Generally, this method of passive stabilisation is applied to aminodiphenylamines, which produce blue and black pigments. A solvent-free and efficient method of diazotisation and coupling using silica sulphuric acid is reported in the literature (Zarei *et al.*,



19.7 Stabilisation using suitable stabiliser.



2009). Using this technique, different types of aromatic amines were rapidly converted to the corresponding azo dyes in good yield. The ensuing aryldiazonium salts supported on silica sulphuric acid (aryl diazonium silica sulphates),  $\text{ArN}_2^+ \text{^-OSO}_3\text{-SiO}_2$ , were found to be sufficiently stable at room temperature in the dry state. Improvement in the stability of the diazonium species through nano scale encapsulation in the cavity of a suitable host is reported by Brumaghim *et al.* (2004). Encapsulation in the protected environment of the host cavity alters the reactivity of the guest molecules, giving them greater stability.

### 19.8.3 Important points regarding the developing bath

The stability of the hydrochloride acid solutions of diazotised fast colour bases is reduced after neutralisation with acetate for development. Hence neutralisation of the acidic solution should be conducted just before use. Similarly the fast colour salts should only be dissolved just prior to use. Addition of a non-ionic dispersing agent keeps the loose pigments formed in the dispersed state and helps to obtain better rubbing fastness of the dyed substrate. Fatty alcohol polyoxyethylene types of non-ionic dispersant are suitable for this purpose. It is always recommended not to store the developing bath for long but if necessary, it should be stored in a cool and dark place. Unlike the naphtholate solutions, which must always be prepared with soft water, hard water can be used for the preparation of the developing bath.

### 19.8.4 Coupling

The moment the naphtholated material is introduced into the developing bath, precipitation of the azoic dye begins. The reaction is called coupling (Christie, 2001, p. 56). In practice some time is required for the completion of coupling reaction. Thus a bright yellow pigment is formed when a cotton fabric naphtholated with Naphthol AS is coupled with diazotised Fast Yellow GC base.

There is considerable variation in the rate at which coupling takes place with different bases and fast colour salts, and the rate of reaction can be controlled by pH. The diazo components are divided into four groups according to their coupling energies and specific pH ranges at which the reaction proceeds.

#### *Group 1*

High coupling energy, optimum pH range 4.0–5.5. No buffer is necessary, but an alkali-binding agent is essential.

- (a) Rapid coupling rate C.I. Azoic Diazo Components 6, 7, 3, 37, 9.
- (b) Medium coupling rate C.I. Azoic Diazo Components 44, 2, 18, 18, 16, 12, 13, 34, 8, 36.
- (c) Slow coupling rate C.I. Azoic Diazo Components 19, 50, 5, 4, 38, 49, 17, 1, 27, 21.

### *Group 2*

Medium coupling, optimum pH range 5.0–6.5. Acetic acid – sodium acetate buffer is necessary to maintain pH.

- (a) Rapid coupling rate C.I. Azoic Diazo Components 40, 30.
- (b) Medium coupling rate C.I. Azoic Diazo Components 26, 33, 29, 39, 32, 11, 10.
- (c) Slow coupling rate C.I. Azoic Diazo Components 31, 42, 25.

### *Group 3*

Low coupling energy, optimum pH range 6.0–7.0. The bath should be neutralised with sodium bicarbonate, then buffered with mono- and di-sodium phosphate buffer mixture (4 and 2 g/L respectively for a liquor ratio 1:20, double and four times the quantities for liquor ratios 1:10 and 1:5, respectively).

- (a) Rapid coupling rate C.I. Azoic Diazo Components 43.
- (b) Medium coupling rate C.I. Azoic Diazo Components 41, 20, 24, 45.
- (c) Slow coupling rate C.I. Azoic Diazo Components 15.

### *Group 4*

Very low coupling energy, optimum pH range 7.0–8.2. The members belonging to this particular group may have different rates of coupling and accordingly those are subclassified as rapid, medium and slow coupling rates. If the pH of the developing solution is changed considerably for some reason, coupling reaction may not take place completely. Too high a pH retards coupling and speeds up decomposition of the diazonium salts.

Although azoic combinations are used for continuous dyeing 100% cellulosic fabrics, they are, perhaps surprisingly, more widely used for continuously dyeing polyester/cotton fabrics. This requires that the goods be run twice with the disperse dye being applied to the polyester and reduction cleared in the first pass and naphtholation and coupling being conducted on the second pass. Dabbagh *et al.* (2007) revealed the use of some environmentally friendly clay catalysts for diazotisation and diazo coupling reactions. These catalysts are claimed to be reusable and non-corrosive.

The dyeing of cellulosic fabrics by simultaneous application of azoic components and vinylsulphone or monochlorotriazine reactive dyes is reported by Ethirajan (1994).

## 19.9 After-treatment

After-treatment includes rinsing, acidification, after-development and alkaline soaping, followed by rinsing. Boiling with alkaline soap liquor results in crystallisation of the major portion of insoluble azoic dye within the fibre and only a small amount remains loosely adhered to the fibre surface. After acidification the material is given a cold rinse and then treated in a bath containing alkaline soap (3 g/L) and soda ash (1–2 g/L) at 70–80°C for 10–15 min. For hard water areas a water softening agent should be used. This is followed by treatment in a second bath containing 1–2 g/L non-ionic dispersing agent at 70–80°C for 10–15 min. Final cold water rinsing completes the process.

The dyes present in the interior of the fibre undergo reorganisation or crystallisation during soaping which increases the intermolecular interaction forming aggregates of the pigment. The increased compactness of the crystalline structure acts as a protective agent against the attack by external agencies, thus improving the fastness of the pigment.

## 19.10 Dyeing of silk

Silk is less sensitive to dilute alkalis but when treated with strong hot alkalis silk fibre dissolves. Silk can be naphtholated in the same manner as used for wool. But naphthols have lesser affinity to silk, hence for darker shades salt is required to be added and the treatment time should also be increased for good exhaustion. The diazotised bases couple with the silk fibre itself, in addition to the naphthols present in the fibre. This causes a yellowing effect after development. The dyed material after development is soured with dilute hydrochloric acid, rinsed and finally subjected to a hot soaping treatment.

## 19.11 Dyeing of polyester

Generally polyester is not dyed using azoic colours. However, azoic colouration technology may be employed for obtaining heavy shades on polyester such as black, deep maroon, red shades, etc. The method used in this case is different from the usual method of producing *in situ* azoic pigments within the fibre. Polyester is boiled in an aqueous dispersion of naphthol and the base and subsequent development is carried out by impregnation into hot nitrous acid. Otherwise a ‘reversed azoic process’ may be used, in which

the application of the base is followed by naphtholation and development (Whittaker *et al.*, 1964). Naphthols and aromatic amines have adequate diffusional behaviour within the polyester fibre.

### 19.12 Dyeing of nylon

Like polyester, nylon can also be treated with both naphthol and base at 85–90°C followed by the diazotisation operation at a lower temperature such as 12–15°C. Azoic colours give good coverage of both physical and chemical variations in the fibre. The wash and light fastness of azoic dyed nylon are also quite good (Douglas, 1951). Azoic shades on nylon are comparatively duller compared to those on cotton; therefore, this process is mainly used for the production of black shades.

### 19.13 Fastness properties

The wash fastness properties of azoic dyed cellulosic materials are excellent. All azoic combinations withstand soaping at the boil. The dark shades exhibit excellent light fastness. However, at medium and pale shades light fastness is good to fair. Like many other dyes the light fastness on azoic dyed ground is also affected by environmental humidity. Unlike sulphur dyes most of the azoic pigment withstands chlorine bleaching. In India, for example, azoic dyed coloured yarns are used for borders during weaving cheaper quality materials especially saris. These woven fabrics may be bleached with chlorine containing bleaching agents without any danger of colour removal. Most of the azoic combinations have excellent perspiration fastness also. Fastness to hydrogen peroxide is not adequate. Many organic solvents affect most of the azoic dyed shades. Rubbing fastness problems are very common with azoic colours, although as discussed earlier, this problem can be overcome by adopting proper dyeing technology (see Section 19.7). Generally the tone of azoic dyed ground is not affected by the post-dyeing/finishing operations such as resin finishing (Chattopadhyay and Kaushik, 1994). The dischargeability of azoic colours is good; hence they are suitable for dyed ground shades intended for white or coloured discharge prints. The use of azoic colours has declined since the introduction of reactive dyes and the subsequent developments of this dye class.

### 19.14 Stripping of azoic colours

Azoic colours from azoic dyed cellulosic textiles can be removed with the help of strong reducing agents. The method involves the conversion of the chromophoric azo group to almost colourless amino groups. The coloured pigments are thus destroyed by reductive cleavage of the azo group. The

remaining amines should be removed by thorough washing since they can be oxidised in air which will again form coloured compounds. Azoic dyeings can be stripped from cellulosic materials with 5–10 mL/L caustic soda (27% by weight), 3–5 g/L sodium hydrosulphite and 1–2 g/L some dispersing agent. An addition of a little anthraquinone (0.5 g/L) enhances the reduction process. Stripping liquor turns red on addition of anthraquinone. If the liquor turns yellow or brown a further addition of reducing agent must be made. Stains developed on the fabric during stripping should be removed by thorough hot and cold washing. Removal of colour from naphtholated material before development is easier than stripping a developed colour.

### **19.15 Environmental issues associated with azoic colours**

In 1994, the German government banned the use of some azo dyes that yield, on reduction, any of the twenty arylamines, including benzidine and its disubstituted congeners. Following the German ban in 1994, several other European community countries (EU member states) introduced similar regulations. According to EU Directive 2002/61/EC twenty-two amines are banned (Table 19.3). Developing agents are all diazotisable amines or diamines or substituted anilines, toluidines, anisidines, azobenzenes or diphenylamines. Many of these chemicals are under eco-pressure (Chattopadhyay and Kumar, 2001).

2-Naphthylamine is known to be a human carcinogen based on sufficient proof of carcinogenicity in humans. Various diazo components which are known to be carcinogenic and prohibited are Fast Red TR Base (Azoic Diazo Component 11, C.I. 37085), Fast Scarlet G Base (Azoic Diazo Component 12, C.I. 37105), Fast Red GTR Base (Azoic Diazo Component 29, C.I. 37255), Fast Blue B Base (Azoic Diazo Component 48, C.I. 37235), Fast Blue Corinth B Base (Azoic Diazo Component 112, C.I. 37225), Fast Dark Blue R (Azoic Diazo Component 113, C.I. 37230), Fast Orange R Base (Azoic Diazo Component 7, C.I. 37270), Fast Blue BB Base (Azoic Diazo Component 20, C.I. 37175), Fast Blue RR (Azoic Diazo Component 24, C.I. 37155) and Fast Violet B Base (Azoic Diazo Component 41, C.I. 37165) (Aspland, 1997; [http://ns.ist.cmu.ac.th/riseat/documents/a\\_dyes.pdf](http://ns.ist.cmu.ac.th/riseat/documents/a_dyes.pdf)).

Workers engaged in diazotisation of these amines are exposed to the flying dust of these carcinogenic chemicals. The powders deposit on the body and also enter the body through inhalation. Hence the workers using harmful amines in the textile industry or dye manufacturing units are at high risk. 5-nitro-o-anisidine is widely used to produce an azo scarlet pigment. Generally, this is not considered to be a harmful amine. However,

**Table 19.3** List of banned aromatic amines according to the EU Directive 2002/61/EC

No	Substance	CAS number
1	4-aminodiphenyl	92-67-1
2	Benzidine	92-87-5
3	4-chloro-o-toluidine	95-69-2
4	2-naphthylamine	91-59-8
5*	4-amino-2',3'-dimethylazobenzene	97-56-3
6*	2-amino-4-nitrotoluene	99-55-8
7	4-chloroaniline	106-47-8
8	2,4-diaminoanisole	615-05-4
9	4,4'-diaminodiphenylmethane	101-77-9
10	3,3'-dichlorobenzidine	91-94-1
11	3,3'-dimethoxybenzidine	119-90-4
12	3,3'-dimethylbenzidine	119-93-7
13	3,3'-dimethyl-4,4'-diaminodiphenylmethane	838-88-0
14	4-cresidine	120-71-8
15	4,4'-methylene-bis-(2-chloroaniline)	101-14-4
16	4,4'-oxydianiline	101-80-4
17	4-4'-thiodianiline	139-65-1
18	2-aminotoluene	95-53-4
19	2,4-diaminotoluene	95-80-7
20	2,4,5-trimethylaniline	137-17-7
21	2-methoxyaniline	90-04-0
22**	4-aminoazobenzene	60-09-3

\*Amines 5 and 6 are analysed indirectly via reduction to the amines 18 and 19, respectively.

\*\*No analytical procedure is currently available for 4-aminoazobenzene.

the pigment on reduction will produce 2,4-diaminoanisole (4-methoxy-m-phenylene diamine), since both the azo and nitro groups of the pigment are reduced to amino groups. This diamine is a known harmful amine. The reductive enzymes present in the body such as NaDPH-cytochrome reductase and cytochrome-450 can reduce the azo and amino groups. C.I. ACC 7 is also forbidden. Peterson *et al.* (1990) published the dermatological effect of Naphthol AS (ACC 2).

Since many of the components used in naphthol dyeing are known or suspected carcinogens, they should not be used. During selection of an ACC and azoic diazo component care should be taken and it is advisable to consult Safety Data Sheets for the materials. Besides these fast bases there are other bases or their salts which are also harmful and should not be used; these include Fast Yellow GC Base (<http://actrav.itcilo.org/actrav-english/telearn/osh/ic/95512.htm> [accessed 16 February 2010]), Fast Red A1 salt ([http://msds.chem.ox.ac.uk/FA/fast\\_red\\_A1\\_salt.html](http://msds.chem.ox.ac.uk/FA/fast_red_A1_salt.html) [accessed 16 February 2010]), Black K salt ([http://msds.chem.ox.ac.uk/FA/fast\\_black\\_k\\_salt.html](http://msds.chem.ox.ac.uk/FA/fast_black_k_salt.html)

[accessed 16 February 2010]) and Fast Red violet diazonium salt (Woods and Ellis, 1994).

## 19.16 Conclusion

Dyeing with azoic colour is mostly employed for cellulosic materials with good to excellent fastness properties and good economy. It is suitable for producing dark shades such as scarlet, red, navy blue, orange and maroon. For the application of azoic colour the various steps to be followed are (a) selection of appropriate combination; (b) dissolution of naphthol by a suitable method and (c) selection of naphtholation technique and determination of the amount of naphthol required. Most of the naphthols have poor exhaustion property. Naphthols with high substantivity should be used in the batch process and a standing bath should be used to utilise the unexhausted naphthols. For pad application it is better to use naphthols of low substantivity; (d) removal of excess naphthol from the textile materials by a suitable technique; (e) amount of fast base or fast salt required to be calculated from the coupling ratio of the coupler and the diazo component. Manufacturers' instructions should be followed when (f) the base is to be diazotised by a suitable method; (g) development of the colour as discussed earlier with all precautions; and finally (h) after-treatment. Material data sheets should be consulted before selecting an ACC and azoic diazo component.

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