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Kübra Güneş
M. Sadi Gürses

Dyes and Pigments

Springer

SpringerBriefs in Molecular Science

Green Chemistry for Sustainability

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Kübra Güneş · M. Sadi Gürses

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Ahmet Gürses
Kazım Karabekir Eğitim Fakültesi
Atatürk Üniversitesi
Erzurum
Turkey

Metin Açıkyıldız
Kilis 7 Aralık University
Kilis
Turkey

Kübra Güneş
Atatürk University
Erzurum
Turkey

M. Sadi Gürses
Koç University
Istanbul
Turkey

ISSN 2191-5407 ISSN 2191-5415 (electronic)
SpringerBriefs in Molecular Science
ISSN 2212-9898
SpringerBriefs in Green Chemistry for Sustainability
ISBN 978-3-319-33890-3 ISBN 978-3-319-33892-7 (eBook)
DOI 10.1007/978-3-319-33892-7

Library of Congress Control Number: 2016938383

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG Switzerland

Preface

Nowadays, dyes and pigments are of great interest in terms of scientific research and practical applications. This book has been written to create the concise practical overview of colorant substances by offering a comprehensive introduction devoted to the historical development of dyes and pigments.

In this context, Chap. 1 is devoted to the historical development of dyes and pigments. Chapter 2 predominantly examines the structures of dyes and pigments with the formation mechanisms of color and the chemistry of dyes. Hence, this chapter starts with the brief information about the chemical structures of typical colorants and ends with a comprehensive analysis of the color phenomenon.

The extensive information about different colorants and their structural characteristics has a critical importance in the creation of novel dye types and their application fields and also in the preparation of new dye formulations which cover nanotechnological applications. Therefore, Chap. 3 highlights the differences between dyes and pigments by considering the main classifications of the dyes and pigments.

Chapter 4 is devoted predominantly to the dyeing methods including several modern and traditional techniques.

Finally, in Chap. 5, a wide range of dyes and pigments are discussed in the context of green chemistry with environmental and health aspects by considering their negative results related with their use.

To sum up, this book is a detailed review particularly about dyes, pigments, and color, and even paints.

We believe that this book containing many figures, schemas, and numerous relevant references in each chapter would be an essential reference source for the readers working on the researches and applications related to dyes, pigment, and dyeing.

Erzurum
2016

Ahmet Gürses
Metin Açıkyıldız
Kübra Güneş
M. Sadi Gürses

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Chapter 1
Historical Development of Colorants

Abstract Color is one of the elements of nature that makes the human life more aesthetic and fascinating in the world. Plants, animals, and minerals have been used as primary sources for colorants, dyes or pigments since ancient times. The first fiber dyes known to be used in prehistoric times consisted of fugitive stains from berries, blossoms, barks, and roots. This chapter is devoted to an historical introduction to the colorants, taking into account of the chronological developments in dyeing processes and the origins of dyes used. Even today, the dyeing using natural materials is applied as an adjunct for hand spinning knitting and weaving but it has remained as a living craft in many traditional cultures of North America, Africa, Asia, and the Scottish Highlands. The new discoveries about the science of color have also led to many industrial innovations and a sharp fashion change. Scale insects have long been used to produce crimson-colored dyes. Many plant pigments are used as dyes. Madder has been utilized since times as a red vegetable dye for leather, wool, cotton and silk. Indigo is a natural dye that is structurally related to betalains. Tyrian purple, which is an ancient dye, has been extracted from shellfish of the Murex genus.

Keywords Natural dyes and pigments · Madder · Murex · Tyrian purple · Kermes · Cochineal · Woad · Indigo · Mauveine · Lapis lazuli

1.1 Introduction

In recent years it is observed an increased interest to dyes that are derived from natural sources, especially among artists working on textiles (Sequin-Frey 1981). This chapter provides an historical introduction to the colorants, taking into account of the chronological developments in dyeing processes and the origins of dyes used.

Plants, animals, and minerals were known as the primary sources for colorants, dyes or pigments, until the middle of the nineteenth century (Vankar 2007). The first fiber dyes known to be used in prehistoric times consisted of fugitive stains from berries, blossoms, barks, and roots (Das 2011; Sharif 2007). They are early examples

A. Gürses et al., *Dyes and Pigments*, SpringerBriefs in Green Chemistry for Sustainability, DOI 10.1007/978-3-319-33892-7_1

of direct dyes or substantive dyes that can give color to the natural fiber without specific pre-treatment onto the dyeing material or the textile. However, the dyeing process itself was simple but has exhibited rather limited color fastness, i.e. a poor resistance for color-change after repeated washings or after exposure to light (Mussak and Bechtold 2009). Therefore, examples of prehistoric dyes have only been found in rare situations, where the colors and fibers were preserved by permafrost or dry desert sand or under the anaerobic conditions of a swamp. In later times, more complicated dyes and advanced dyeing procedures capable of producing the colors with better fastness have been developed (Samanta and Konar 2011).

As a typical vat dye, indigoid dye is probably the oldest natural dye used by man. It is found as the glucoside indicant in the plant *Indigofera tinctoria* and has been known in India for about 4000 years (Samanta and Agarwal 2009). After the treatment with urine followed by the fermentation of the plant; dyeing has been carried out by dipping the fibers into the colorless dye bath and by drying them in the sun to get blue, insoluble dye in the surface of the fiber (Wisniak 2004). Phoenician traders and migrants introduced this dye to the Mediterranean area and then its use gradually spread to the whole Europe.

The most important another source of blue colorants in Europe was also Woad, *Isatis tinctoria*, used since the Bronze Age (2500–800 BCE), from which chemical indigo could be produced (Cortat et al. 2007; Schaefer 2014). However, due to by products, the resulting blue is not as pure as that from the indigo plant. In the 1500s, indigo was imported for high prices to Northern Europe (Sequin-Frey 1981). In spite of a decree prohibiting import of indigo in order to protect local woad growers in England, indigo had monopolized completely the market in 1740s (Nash 2010).

Tyrian purple, which has been derived from the shell fish of the genera, Purpura and Murex, is a well-known example of ancient vat dyes (Melo 2009). Tyre and Sidon, where are the Phoenician towns, have been the center of this dye industry around 800 BCE (Rondão 2012).

Many shades of red have been created with the madder root derived from the Mediterranean and Asian plant, *Rubia tinctorum*. Alizarin and purpurin are extracted from Madder root, which first appeared in Italy A.D. 1291 (Rogers 2005; De Santis and Moresi 2007).

Many colorants do not have strong chemical affinity for the textile fibers. Therefore textile fibers are required to treat before the dyeing stage involving a two-step chemical reaction. A solution of a mordant, typically a metal salt, is first used to impregnate the fibers. It allows the metal ion to form the complexes with appropriate functional groups in the structure of the textile. Aluminum, iron, tin, chromium or copper ions, as well as tannins are examples of mordants. Potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$), also known as potash alum or aluminum potassium sulfate was one of the most common substances in ancient times, but iron sulfate ($FeSO_4 \cdot 7H_2O$) and ($SnCl_2$) were often used as well (Pozzi 2011). In ancient times, mordanting was achieved by carrying out the dyeing process in copper or tin containers, or by adding iron nails. Already, the most of natural dyes are also involved in the group of mordant dyes. Kermes and lac that are red mordant dyes are the known oldest insect dyes. First of them (the scarlet red dye) is extracted from the insect, *Kermes ilicis* and the other is also extracted from the insect, *Coccus lacca* found in India and Southern Asia (Kapoor et al. 2008).

Ancient dyes and dye procedures have been recorded mainly by two famous historians of the first century. In his writings the Roman naturalist Pliny the Elder refers to indigo and woad as a common dye used among Gallic tribes. The Greek physician Dioscorides describes the dyes of madder for red, saffron (from the stigmas of *Crocus sativus*) for yellow, weld (from *Rseda luteola*) for yellow, woad for blue, and dyers' bugloss (*Alkanna tinctoria*) for red. Barks of oaks, walnut hulls, and oak galls, which are rich in tannins, have been used to provide dye and mordant as well as to create colors from brown to black (nicDhuinnshleibhe 2000). Until the 1250s, the well-developed many dye procedures had been recorded by medieval monks. Back then, dye plants and herbs of medicinal usage were often similar. The preference toward to the particular dyes depended highly on the local availability of the corresponding plants. As the medieval trade unions grew, they took over the tradition of dye procedures. Many dyers' guild carried the saffron crocus in its coat of arms. Dye procedures developed further and kept as highly guarded secrets. Famous centers of dye production and trade were Venice, Florence, Genoa, Basle, Frankfort, Nuremberg, Antwerp, and London. Saffron, madder, indigo, woad, and other dyes, and dye ingredients had possessed a great commercial value at medieval markets.

The famous historical recording named Plictho de Larti de Tentori, written by Giovanni Ventura Rosetti, gives the detail information about the dye and dyeing procedures applied by the Venetian dyers' guild (Dutton 1992).

Early pueblo dwellers living in the Southwest region of the North America were quite master in the arts of fiber and dyeing. After the discovery of the American contınent, many dyes such as, the deep-yellow fustic derived from *Chlorophora tinctoria*, as well as *logwood*, *Haematoxylon campechianum*, were exported to Europe (Ojha 2011). However, the most important one of the exported dyes was cochineal, or carmine red, prepared from the dried cactus insects of Coccus cacti (Nejad and Nejad 2013).

The first dyers' handbook published in America, The Dyer's Assistant is written by Asa Ellis in 1798. In 1930, it has been started a program to revive ancient fiber crafts among Indians in America, and thus so far, the tradition of dyeing with natural products has been conserved by Hopi and Navajo Indians (Collier and Strong 1936).

1.2 Origins of Natural Dyes

The colorants that impart color such as pigment, dye, ink, and paint are generally derived from plant, mineral or invertebrates. The majority of natural colorant substances are the dyes deriving from plant sources (roots, berries, bark, leaves, and wood) and other organic sources such as fungi and lichens. Archaeological researches have shown that the onset of textile dyeing can be back the Neolithic period.

In China, dyeing with plants, barks and insects has been traced back more than 5000 years (Naik et al. 2013).

Colors in the *ruddy* range consisting of red, brown and orange are the first attested ones in many ancient textile sites, across the Levant, Egypt, Mesopotamia and Europe. The evidences for blue, yellow, and green colors have been obtained later. The earliest surviving evidence of textile dyeing has been discovered at the large Neolithic settlement at Çatalhöyük in Central Anatolia (Turkey), where was found the traces of red dyes probably originated from *ochre* (iron oxide pigments from clay) (Şare 2011).

Nevertheless, it is estimated that polychrome or multicolored fabrics appeared in the 3rd or 2nd millennium BCE. The textiles consisting of a red-brown warp and an ochre-yellow weft which were discovered in Egyptian pyramids (2345–2180 BCE) are the known first samples (Muniapan 2013).

The chemical analysis that can identify the dyes used in the ancient textiles has rarely been achieved and even if any dye is detected. It has not been possible to determine which of same dye-bearing plants was used. Nevertheless, based on the colors of surviving textile fragments and the evidence of actual dyestuffs found in archaeological sites, it can be claimed that reds, blues, and yellows from plant sources were in common use in the late Bronze Age and Iron Age (Godlove 2011).

Many different plants, including many lichens, henna, alkanet, or bugloss (*Alkanna tinctoria*), asafetida and madder can be used to produce red dyes. Madder (*Rubia tinctoria*) and related plants of the *Rubia* family are native to many temperate zones around the world and have been used for dyeing of the textile fibers such as wool or silk in many parts of the world since ancient times (Karadag and Dolen 2007; Derksen et al. 2004). Madder has been a dye of commercial importance in Europe through the many years, and was used commonly in Holland, France and England until its market collapsed with the development of synthetic alizarin dye in 1869 (Lopez 1989).

The aluminum mordant of alizarin that is obtained from the root of the *rubia* plant by a multistep complicated process appeared in India is the well-known strong red dye named as Turkey red. It utilized to dye cotton and wool with excellent fastness. After in 1784, a different version of Turkey red is produced in England, roller-printed cotton clothes dyed with this dye have been the fashion items of 1800s there (Tuckett and Nenadic 2012).

Indian madder (*Rubia cordifolia*) known also as Munjeet is particularly native to the Himalayas and is an important dye for the Asian cotton industry (Gleba et al. 2015). Bloodroot is a popular red dye used for dyeing among Southeastern Native American people. The most common name of it was *Sanguinaria canadensis*. The commonly known other names of this dye can be listed as red puccoon, tetterwort, redroot, pauson, turmeric, sweet slumber and Indian paint (Braly 2007). The staghorn sumac, prickly pear cactus, *Opuntia polycanthathe*, and water oak, *Quercus nigra,* have been used by the other Native American people such as the Coushatta, the Choctaw, and the Navajo to produce different red dyes. In addition, Navajo dyers created orange dyes by using one-seed juniper, *Juniperus monosperma*, Navajo tea, *Thelesperma gracile*, or alder bark (Wheat 2003).

Yellow dyes can be extracted from saffron, pomegranate rind, turmeric, safflower, onion skins, and a number of weedy flowering plants (Barber 1991; Goodwin 1982). For before the Iron Age, the evidence about the use of weed, *Reseda luteola* is limited but the weld called also *mignonette* (or *dyer's rocket*) being an important dye for the same period in the ancient Mediterranean and Europe was used to produce the yellow dye (Mahanti 2011). The two brilliant yellow dyes with commercial importance in Europe in the 18th century have been obtained from the inner bark of the oaks (quercitron) native to the North America, with the dyer's mulberry tree, *Maclura tinctoria* (fustic) native to the West Indies and Mexico (Saunders 1920).

Butternut (*Juglans cinerea*) and yellow root (*Xanthorhiza simplicissima*) that could give a rich yellow color have been used by the Southeastern tribes (Bose and Nag 2012). Butternut bark and nut rinds were once often used to dye cloth to colors between light yellow and dark brown. The plants such as, small snake-weed, brown onion skins, rubber plant, *Parthenium incanum*, Rabbit bush, *Chrysothamnus*, and rosehips have also been used to create yellow colored dyes by Navajo tribe.

Woad and indigo, which can give blue color, have been used since ancient times in combination with yellow dyes to produce shades of green. The once famous Kendal green was wool dyed yellow with greenweed and overdyed with woad or indigo. However, it lost its popularity after the production of the brighter Saxon green, obtained with indigo and fustic in the 18th century.

Soft olive greens are also achieved, when textiles dyed yellow are treated with an iron mordant (Chakraborty 2014). The dull green cloth that was native to the Iron Age Halstatt culture bears traces of iron, probably originating from the manufacturing process.

The Indigenous peoples in the Northwest Plateau in North America used lichen to obtain a beautiful sea green. Moreover, red onion skins were used by Navajo dyers to produce green color.

Indigo is a natural, dark blue dye obtained from the *Indigofera tinctoria* plants native to India, Java, and other tropical areas (Derrick et al. 1999; Sloane 1989). Therefore, India is referred as the oldest indigo dyeing center in the Old world. On the other hand, it is known that the main two blue dyes used in Central and South America were Anil indigo (*Indigofera suffruticosa*) and Natal indigo (*Indigofera arrecta*) (Bose and Nag 2012). Indigo had been obtained from woad (*Isatis tinctoria*) predominantly, in all the temperate climate areas including of Europe (Vajanto 2015).

Woad is a natural indigo-producing plant in Europe. Apart from this, dyers knotweed (*Polygonum tinctorium*) and West African shrub (*Lonchocarpus cyanescens*) are some of the plants used to produce indigo traditionally. The use of natural indigo started declining after the manufacture of synthetic indigo (Saxena and Raja 2014).

In medieval Europe, purple, violet, murrey and similar colors were produced by using woad or indigo and red dyes such as madder, or kermes and cochineal. In addition, madder can produce purples by using alum and purple shades obtained by utilizing *Brazilwood* with vitriol (sulfuric acid) or potash. Maple, *Acer* sp., for producing lavender and purple dyes has been used traditionally by Choctaw Indians.

Furthermore, purple dyes can be derived from lichen as well as the berries of White Bryony and mulberry (*morus nigra*) (with an acid mordant) (Goodwin 1982). Cutch is an ancient brown dye and is extracted from several species of Acacia (especially Acacia catechu, or Senegalia catechu). This dye could give gray-browns and olive-browns, using the iron and copper mordants and it was used commonly in India for dyeing cotton for over 2000 years (Abdel-Kareem 2012).

Historically, the bark of black walnut was used by several Native Americans, including the Cherokee, Delaware, Iroquois, and Meskwaki. The Cherokee, Chippewa, and Meskwakis' people also used the bark to make a dark brown or black dye. Juniper, Juniperus monospermas' ashes were also used to produce brown and yellow dyes by Navajo people (Moerman 1998). Moreover, a black dye with mineral yellow ochre mixed with pitch from piñon tree (*Pinus edulis*) and three-leaved sumac (*Rhus trilobata*). A cool grey dye from blue flower lupine and a warm grey dye from Juniper mistletoe (Phoradendron *juniperinum*) were produced by Navajo's people.

Dye-bearing lichens produce a wide range of greens, oranges, yellows, reds, browns, and bright pinks and purples. The lichen (*Rocella tinctoria*), which is common along the Mediterranean coasts, was used by the ancient Phoenicians. The use of orchil, which is called also as archil and could give a violet coloring matter, started in the Mediterranean area but it quickly has spread through Europe (Zanoni and Schofield 1983). Nowadays, lichen dyes form an important part of the traditional dyes in Wales, Ireland, Scotland, and among native people of America. *Cudbear* and *crottle* are known as Scottish lichen dyes.

Miriam C. Rice, who is the pioneer of researches on the use of various mushrooms dyes, discovered the wide spectrum of mushroom dyes (Krebill 2010). Based on her researches, Swedish and American mycologists have discovered novel sources for true blues (*Sarcodon squamosus*) and mossy greens (*Hydnellum geogenium*). *Hypholoma fasciculare*. Mossy green is a common woodland mushroom known as the sulfur tuft, or clustered woodlover. It could provide a yellow dye. *Pisolithus tinctorius* (Dyer's puffball) and *Phaeolus schweinitzii* (Dyer's Polypore) are used in dyeing textile and paper (Beebee 2008).

Biological pigments were often difficult to acquire and the details of their production were kept secret by the manufacturers. For example, Tyrian purple, which was a pigment, is a purple-red dye extracted from various genera of sea snails. Around 1500 BC, the ancient Phoenicians discovered to obtain a deep violet color for the textile dyeing from the secretions of some Mediterranean sea snails (Głowacki et al. 2012).

Tyrian purple, also known as Royal purple, shellfish purple and Purple of the Ancients, is a well-known colorant obtained solely from muricids. It has been used since antiquity on at least three Continents (Europe, Asia and the Americas) (Benkendorff et al. 2004). Tyrian purple that was used for imperial manuscripts on purple parchment often with text in silver or gold retained its place for a long time as the premium dye of Europe until it replace with the rich crimson reds. Therefore, the garments dyed by using this pigment have been accepted the sign of power and wealth (Krafts et al. 2011).

Murex (*Bolinus Brandaris*) is known as one of the most valuable dyes in the antique period which exhibits high resistance to fading and could give the brighter and more intense colors with sunlight. The heaps of crushed murex shell found in the many settlements in the eastern Mediterranean dated to 1500s BCE suggest that the first Murex dyeing was made by the East Crete people or the West Semites along the Mediterranean coast (Schneider 2012). Phoenician red produced from the Murex snails with a very low yield, which is called also as classical dye, is the extremely valuable murex dye.

Kermes is extracted from the insects, (*Kermes vermilio* or *Kermococcus vermilio*), which live on species of oak especially in the Mediterranean region (Karalı and Megaloudi 2008). Kermes dyed jars found in a Neolithic burial cave also indicate the ancient origin of Kermes. This type dyes are also obtained from the insects, *Porphyrophora hamelii* in the Caucasus region and *Coccus polonicus* in Eastern Europe as well as the lac-producing insects of India, Southeast Asia, China, and Tibet (Vajanto 2015). Until the middle of the 11th century, the dyestuffs had been called as “grain” in all Western European languages. Kermes dyed textiles had also been described as “dyed in the grain”.

Cochineal (*Dactylopius coccus*) that could give the crimson-colored carmine dye used by the Aztec and Maya people is an insect found in Central and North America (Chattopadhyay et al. 2008). After the conquest by Spanish of the Aztec Empire, cochineal began to be exported to Spain. During the colonial period, the production of cochineal grew rapidly. Indigenous producers cultivated Cochineal exclusively in Oaxaca. It had become Mexico’s second most valued export product after silver. Cochineal that is mordanted with tin and used in smaller quantities with the brilliant scarlet colors has replaced of kermes dyes being in general use in Europe from the 17th century (Etkin 2008).

The production of fast black in the Middle Ages has been made using a complicated process. The process involves multiple-dyeing with woad or indigo followed by mordanting. Later, the new and superior dyeing method that uses logwood or bloodwood (*Haematoxylum campechianu*) which are obtained from the species of flowering tree found in southern Mexico and northern Central America for black dye. It then reached Europe by Spanish conquests in the New World. Despite the changes occurring in fashion colors, logwood had remained in widespread use to the end of the nineteenth century (Baker 2011).

Mauveine, known also as aniline purple or Perkin’s mauve, is first synthetic organic dye discovered incidentally by William Henry Perkin in 1856 (Glashow 2002). A modern-day laboratory procedure for the organic synthesis of mauveine contains the dissolving of mixture, consisting of aniline, p-toluidine and o-toluidine in the ratios of 1:1:2 in sulfuric acid and water after the addition of potassium dichromate. Mauveine was the first aniline dye. It has pioneered to the development of the hundreds synthetic dyes and pigments as azo and di-azo compounds providing a wide spectrum of color.

Alizarin red (AR) known also as Mordant Red 11 was initially isolated from the madder genus plants and was used as a prominent red dye throughout history. However, by the end of 19th century, this dye began to be produced synthetically

(Rodrigues et al. 2009). Alizarin is the name of the first natural pigment to be produced synthetically. It means a deep red color with its most common use, but the word “alizarin” is appeared also as a part of the several dye names such as Alizarin Cyanine Green and Alizarin Brilliant Blue.

Naturally occurring pigments such as ochre’s and iron oxides have been used as colorants since prehistoric times. Archaeologists have uncovered evidence that early humans used paints for aesthetic purposes such as body decoration. Two examples include red ochre, anhydrous Fe_2O_3 and the hydrated yellow ochre ($Fe_2O_3 \cdot H_2O$) (Adamu et al. 2013). The pigments and paint grinding equipments dated to 350,000 to 400,000 years ago in a cave near Lusaka–Zambia have even been found (Bin Selamat 2010).

Lapis lazuli was used as semi-precious stone and decorative building stone in Egypt. It was also mainly used to produce a pigment known as ultramarine which can give a deep rich blue. However, there are limited cases found where lapis lazuli powder was used as a pigment (Abdel-Ghani 2009). Moreover, the high-cost of lapis lazuli and other mineral pigments produced from naturally occurring materials paved the way for the emergence of the more cheap alternatives such as mineral (azurite, smalt) and biological (indigo) pigments.

The first two synthetic pigments were white lead (basic lead carbonate, $(PbCO_3)_2$ Pb $(OH)_2$) and blue frit (Egyptian Blue). White lead is made by combining lead with vinegar (acetic acid, CH_3COOH) in the presence of CO_2. Blue frit is calcium copper silicate and was made from glass colored with a copper ore, such as malachite (Emeish 2013).

Prussian blue can be considered as the first modern, totally synthetic pigment, arising as the result of a deliberate chemical reaction without any natural equivalent. The first product was produced accidentally in 1704, but the pigment has achieved a high production level quite soon afterwards (Kirby and Saunders 2004).

By the early 19th century, the many synthetic metallic blue pigments including French ultramarine (synthetic lapis lazuli), Cobalt blue, Cerulean blue and Phthalo Blue (a synthetic organo metallic pigment) had appeared.

In the 1900s, the new strong aniline dyes such as reddish-purple, blue, violet, green, and red dyes began to be used widely and thereby, commercial dyeing with natural dyes was gradually left. The rare and expensive natural dyestuffs began to be out of fashion in Europe in the same century, because in many cases the cost of these dyes has exceeded the costs of the wools and silks (Vettese Forster and Christie 2013).

The new synthetic dyes are more effective on cellulose fibers like cotton, linen. They may be more colorfast on wool and silk. The researches about the production of the aniline dyes have also increased gradually in later years.

Chrome or mordant dyes have provided very wide color range for woolens. After 1875, the acid dyes suitable for animal fibers were produced and in Germany, the synthesis of indigo was carried out. In 1901, the researches about indigo led to the development of a new dye class called as vat dyes which could provide a wide range of colors on plant fibers. In addition, in 1923, the disperse dyes began to be used in dyeing the cellulose acetate textiles. Nowadays, the disperse dyes are the only effective substances for coloring many synthetic materials. The reactive dyes, which appeared in the mid-1950s, have been used also for the craft dyeing together with the commercial textile dyeing. They are generally applied on wool and cotton.

Although the synthetic dyes are popular also among Native American textile artists in America, natural dyes are still in use.

Even today, the dyeing using natural materials is applied as an adjunct for hand spinning knitting and weaving but it has remained as a living craft in many traditional cultures of North America, Africa, Asia, and the Scottish Highlands. The new discoveries about the science of color have also led to many industrial innovations and a sharp fashion change. In addition, the development of chemical pigments and dyes has provided a new industrial prosperity to Germany and the many countries in northern Europe.

Prior to industrialization, many pigments based on mineral and clays were known by the location where they were produced. Historically and culturally, many famous natural pigments were replaced with synthetic pigments, but their historic names have remained. In some cases, the original name has changed its meaning due to conversion of a historic name to a popular modern color. Hence, a contemporary mixture of the pigments that have replaced a historical pigment is named with resulting color, or a hue.

On the other hand, the archaeological researches toward to the historical development of the usage of colorant substances in the form of a paint or paintings have put forward the existence of the 100,000-year-old human-made ochre-based mixtures besides some cave paintings. The cave paintings have been drawn by using red or yellow ochre, hematite, manganese oxide, and charcoal (Hodgskiss 2013). Ancient colored walls found in Dendera-Egypt can be still seen with their brilliant colors as vivid as when they were painted about 2000 years ago (Stanley 2013). It is estimated that the Egyptians were used the six main colors as white, black, blue, red, yellow, and green in ancient times (DeDeo 1999). Paint has been made with the yolk of eggs for hardening and providing of adhesion. Pigment was produced from plants, sand, and different soils. Most paints used either oil or water as a base (the diluting, solvent or vehicle for the pigment).

Oil paints have been used in Europe since the 12th century for simple decoration, but they were not widely adopted as an artistic medium until the early 15th century. Common modern applications of oil paint are utilized in finishing and protection of wood in buildings. They are also used on metal structures such as ships and bridges.

Until the 17th century, oil painting has been made by using a paste consisted of the pigment and oil mixture resulting after grinding by hand with a mortar and pestle. Therefore, the painters have been exposed to the lead poisoning due to the white-lead powder. However, in 1718, Marshall Smith invented a machine grinding pigments in England. This machine increased the grinding efficiency of pigment significantly with its labor-saving technology. By the Industrial Revolution, the paint began to be prepared by grinding in steam-powered mills, and to be used white zinc oxide as an alternative for the lead-based pigments.

Acrylic paints that are fast-drying paint containing pigment suspension in acrylic polymer emulsion are water-soluble but they become water-resistant when dry. As early as 1934, the first usable acrylic resin dispersion has been developed. The synthetic paints combining some of the properties of oil and watercolor have been first used in the 1940s.

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Chapter 2
Dyes and Pigments: Their Structure and Properties

Abstract Dyes and pigments are the most important colorants used to add a color or to change the color of something. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. Dyes are colored substances which are soluble or go into solution during the application process and impart color by selective absorption of light. Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble in, and essentially chemically unaffected by, the vehicle or medium in which they are incorporated. On the other hand, the color, which is highly dependent on the chemical and physical properties of a matter, is a result of the interaction between light and substance. This chapter is focused on the chemical and structural properties of dyes and pigments, as well as the relationship between light and color.

Keywords Dye · Pigment · Colorant · Chromophore · Auxochrome · Color

2.1 Introduction

A color additive is a substance capable of imparting its color to a given substrate, such as paint, paper or cotton, in which it is present. Dyes and pigments are the most important colorants used to add a color or to change the color of something. A dye must be soluble in the application medium, usually water, at some points during the coloration process. It will also usually exhibit some substantivity for the material being dyed and be absorbed from the aqueous solution. On the other hand, pigments are the colorants composed of particles that are insoluble in the application medium (Broadbent 2001). Dyes and pigments as colorants are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. It is estimated that over 10,000 different dyes and pigments are used industrially and over 7×10^5 tons of synthetic dyes are annually produced worldwide (Zollinger 1999; Chequer et al. 2013). The terms, *dye*, *dyestuff*, *pigment*,

A. Gürses et al., *Dyes and Pigments*, SpringerBriefs in Green Chemistry for Sustainability, DOI 10.1007/978-3-319-33892-7_2

color, *colorant*, and *paint* are often wrongly used interchangeably. This chapter focused on the properties of dyes and pigments, chemical and structural considerations, the relationship between light and color.

2.2 Dyes and Pigments

Paint is defined as any liquid, liquefiable, or mastic composition designed for application to a substrate in a thin layer which is converted to an opaque solid film after application. Paint is used for protection, decoration, or identification, or to serve some functional purpose such as the filling or concealing of surface irregularities, the modification of light and heat, etc (Kirk-Othmer 1998a).

Both pigments and dyes are used to provide color to all sorts of substances and have been important to humans since the dawn of history. The difference between the two is that dyes are soluble in the substrate and thus disperse at a molecular level, while pigments are insoluble and are dispersed as particles. Dyes provide brighter color than conventional pigments, but they are less light stable and less permanent (Rothon 2012).

Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble in, and essentially chemically unaffected by, the vehicle or medium in which they are incorporated. They alter appearance either by selective absorption and/or scattering of light. Organic and inorganic pigment powders are finely divided crystalline solids that are essentially insoluble in application media such as ink or paint (Kirk-Othmer 1998b).

Dyes, on the other hand, are colored substances which are soluble or go into solution during the application process and impart color by selective absorption of light. In contrast to dyes, whose coloristic properties are almost exclusively defined by their chemical structure, the properties of pigments also depend on the physical characteristics of its particles (Kirk-Othmer 1998b).

Ever since pre-historic time, man has been fascinated to color the objects of daily use employing inorganic salts or natural pigments of vegetable, animal, and mineral origins. These coloring substances, known as dyes, are the chemical compounds used for coloring fabrics, leather, plastic, paper, food items, cosmetics, etc., and to produce inks and artistic colors. Dyes are of two types, i.e. synthetic and natural. Synthetic dyes are based on petroleum compound, whereas natural dyes are obtained from plant, animal, and mineral matters (Singh and Bharati 2014).

Colorants are normally understood to include both pigments and dyestuff. Pigments refer mainly to inorganic salts and oxides, such as iron and chromium oxides, which are usually dispersed in crystal or powder form in an application medium. The color properties of the dispersion depend on the particle size and form of the pigment. Pigment colorants tend to be the highly durable, heat stable, solvent resistant, lightfast, and migration fast. On the other hand, they also tend to be hard to process and have poor color brilliance and strength. Dyes (also called dyestuff) are conventionally understood to refer to organic molecules dissolved, as molecular

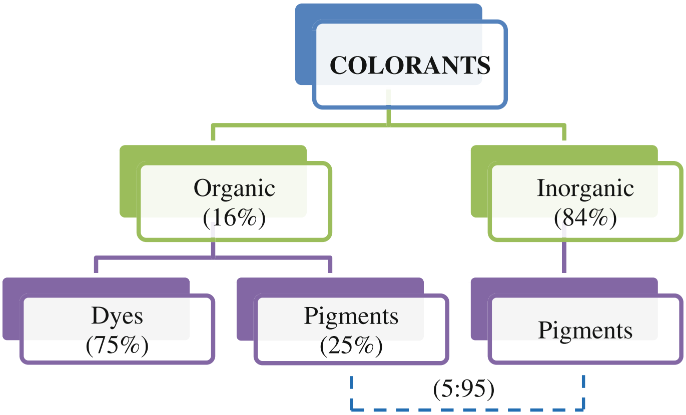


Fig. 2.1 Share of colorants from organic and inorganic classes. Reproduced from Zollinger, Copyright 2003, with permission from Wiley

chromophores, in the application medium. Examples are azo dyes, coumarin dyes, and perylene dyes (Zhang 2010).

Figure 2.1 presents total production amount (weight %) of different classes of colorants (Zollinger 2003; Chakraborty 2010). The global market production of organic colorants in 2010 is forecast to be 2.1 million metric tons valued at 14.4 billion dollars and projected to grow at an annual rate of 3–4 %. The market for inorganic colorants is roughly 5 times larger (Barden 2010).

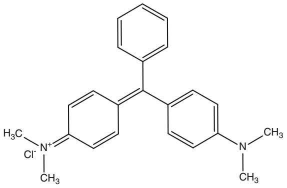
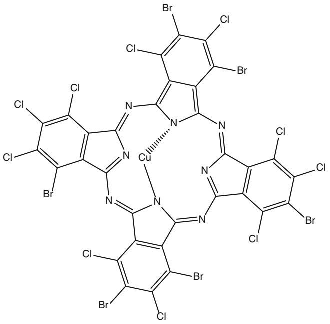
The color imparted by dyestuff to the resulting solution depends on the electronic properties of the chromophore molecule. Dyestuff colorants tend to have excellent brilliance and color strength, and are typically easy to process, but also have poor durability, poor heat and solvent stability, and high migration. Because of the contrasting properties of both types of colorants, much work has been done trying to improve the attributes of each class of colorant. Nanocolorants were regarded as a new class of colorants that could get out of dilemma between dyestuffs and organic pigments. In nature, nanocolorants are a class of nanocomposites that recombine dye acted as an essential ingredient and suitable polymeric matrix, and its performance target is to integrate excellent chromatic properties and good processibility of dyestuffs and good durability of organic pigments. Nanocolorants are new kind of colorants that can combine the advantages of both pigments and dyes, and will be promisingly applied to photoelectric high-tech fields (Zhang 2010).

Dyes can generally be described as colored substances that have affinity to the substrates to which they are being applied (Pereira and Alves 2012). Dyes are soluble and/or go through an application process which, at least temporarily, destroys any crystal structure by absorption, solution, and mechanical retention, or by ionic or covalent chemical bonds (Nwokonkwo 2013). Color Pigment Manufacturers Association (CPMA) has defined pigments as colored, black, white or fluorescent particulate organic or inorganic solids which usually are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light (Merchak 2012).

The key distinction is that dyes are soluble in water and/or an organic solvent, while pigments are insoluble in both types of liquid media. Dyes are used to color substrates to which they have affinity. Pigments can be used to color any polymeric substrate but by a mechanism quite different from that of dyes, in that surface only coloration is involved unless the pigment is mixed with the polymer before fiber or molded article formation (IARC 2010).

The most important differentiation of colorant is that colorant is either dyes or pigment. These terms are often used indiscriminately, in particular, pigments are quite often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied. Pigment particles have to be attached to substrates by additional compounds, for example by a polymer in paint, in a plastic or in a melt. Dyes, on the other hand, are applied to various substrates (textile materials, leather, paper and hair) from a liquid in which they are completely, or at least partly, soluble. In contrast to pigments, dyes must possess a specific affinity to the substrate for which they are used (Zollinger 2003). Some properties of malachite green and pigment green which are important colorants and they are used as coloring agents for different materials were presented in Table 2.1.

Table 2.1 Some properties of malachite green and pigment green 36

	Malachite green (basic green 4)	Pigment green 36 (phthalocyanine green YS)
CAS No	569-64-2	14302-13-7
Chemical structure		
Class	Triarylmethanes	Phthalocyanines
Chemical Formula	$C_{23}H_{25}N_2Cl$	$C_{32}Br_6Cl_{10}CuN_8$
Solubility	Very soluble in water	Insoluble in water
Physical form	Green crystals	Yellowish green powder

2.3 Color and Constitution

The absorption of electromagnetic radiations in the UV and visible regions by a molecule causes to the electronic excitation and an electron moves to higher electronic energy level from a lower. A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, C=C, C≡C, C=O, C≡N, N=N, NO_2 etc. If a compound absorbs light in the visible region (400–800 nm), only then it appears colored. Thus, a chromophore may or may not impart color to a compound depending on whether the chromophore absorbs radiation in the visible or UV region. Table 2.2 shows the some organic dyes and their chromophoric groups (Gangani 2006).

Chromophores like C=C or C≡C having π electrons undergo $\pi \rightarrow \pi^*$ transitions and those having both π and non-bonding electrons, e.g., C=O, C≡N or N=N, undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. Since the wavelength and intensity of absorption depend on a number of factors, there are no set rules for the identification of a chromophore. Characteristics of some common unconjugated chromophores are given in Table 2.3.

A covalently saturated group which, when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as auxochrome, e.g., NH_2, OH, SH, halogens etc. Auxochromes generally increase the value of λ_{max} as well as ε_{max} by extending the conjugation through resonance. These are also called colour enhancing groups. An auxochrome itself does not show absorption above 200 nm. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different values of λ_{max} and ε_{max}. For example, benzene shows λ_{max} 256 nm, ε_{max} 200, whereas phenol shows λ_{max} 270 nm, ε_{max} 1450 (both increased). Hence, OH group is an auxochrome which extends the conjugation involving the lone pair of electrons on the oxygen atom resulting in the increased values of λ_{max} and as $\varepsilon_{max.}$

When two or more chromophoric groups are conjugated, the absorption maximum is shifted to a longer wavelength (lower energy) and usually to a greater intensity compared to the simple unconjugated chromophore, e.g., ethylene shows λ_{max} 171 nm, ε_{max} 15,530 and 1,3-butadiene λ_{max} 217 nm, ε_{max} 21,000. In conjugated dienes, the π molecular orbitals of the separate alkene groups combine to give two new bonding molecular orbitals designated π_1 and π_2, and two antibonding molecular orbitals designated π_3^* and π_4^*. Schema 2.1 shows the $\pi_2 \rightarrow \pi_3^*$ transition, i.e. the promotion of an electron from a highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of a conjugated diene, is of very low energy, 1,3-butadiene shows λ_{max} 217 nm which is lower than the $\pi \rightarrow \pi^*$ transition of an unconjugated alkene, ethylene shows λ_{max} 171 nm.

Similarly, in case of other conjugated chromophores, the energy difference between HOMO and LUMO is lowered resulting in the bathochromic shift. Thus, α,β-unsaturated carbonyl compounds show both $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions at longer wavelengths (e.g., acrolein, λ_{max} 210 and 315 nm) compared to unconjugated carbonyl compounds (acetaldehyde, λ_{max} 180 and 290 nm) (Schema 2.1).

Table 2.2 Some of chromophoric groups present in organic dyes

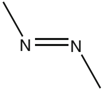
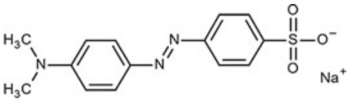
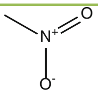
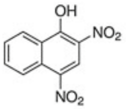
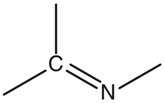
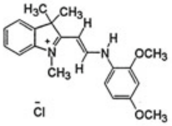
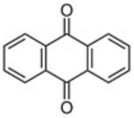
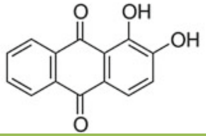
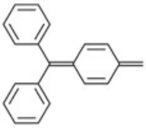
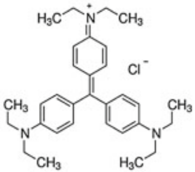
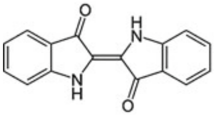
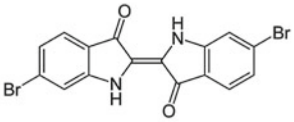
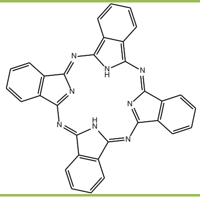
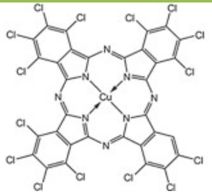
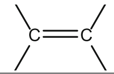
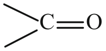
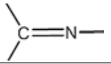
Chromophoric Groups	Sample Dye
	
Azo	Methyl orange
	
Nitro	Martius Yellow
	
Methine	Basic Yellow 11
	
Anthraquinone	Alizarin (Turkey Red)
	
Triarylmethane	Ethyl Violet
	
Indigo	Tyrian purple
	
Phtalocyanine	Pigment green 7

Table 2.3 Characteristics of some common unconjugated chromophores

Chromophore	Example	λ_{max}	ε_{max}	Transition	Solvent
	Ethylene	171	15,530	$\pi \rightarrow \pi^*$	Vapor
$-C\equiv C-$	Acetylene	150 173	~10,000 6000	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Hexane Vapor
	Acetaldehyde	160 180 290	20,000 10,000 17	$n \rightarrow \sigma^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Vapor Vapor Hexane
	Acetone	166 188 279	16,000 900 15	$n \rightarrow \sigma^*$ $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Vapor Hexane Hexane
$-COOH$	Acetic acid	204	60	$n \rightarrow \pi^*$	Water
$-CONH_2$	Acetamide	178 220	9500 63	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Hexane Water
$-COOR$	Ethyl acetate	211	57	$n \rightarrow \pi^*$	Ethanol
$-NO_2$	Nitromethane	201 274	5000 17	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Methanol Methanol
	Acetoxime	190	5000	$n \rightarrow \pi^*$	Water
$-C\equiv N$	Acetonitrile	167	Weak	$\pi \rightarrow \pi^*$	Vapor
$-N=N-$	Azomethane	338	4	$n \rightarrow \pi^*$	Ethanol

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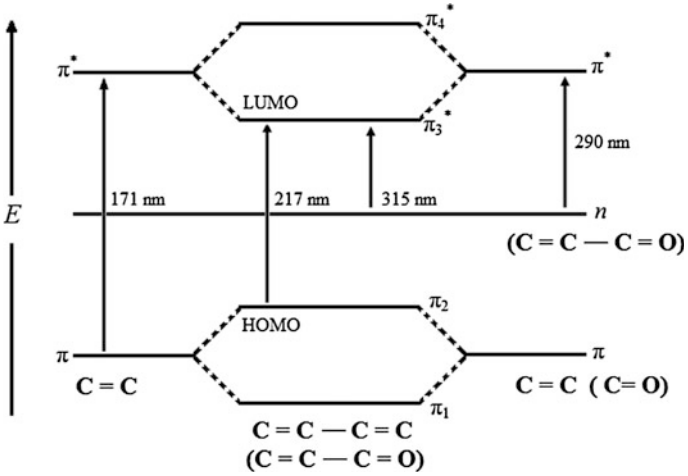
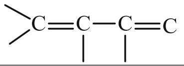
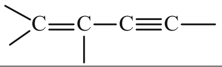
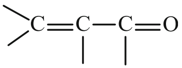
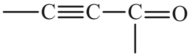
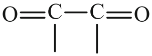


Schema 2.1 Relative energies of electronic transitions in conjugated systems. Reproduced from Yadav, Copyright 2005, with permission from Springer

Table 2.4 Characteristics of some simple conjugated chromophores

Chromophore	Example	λ_{max}	ε_{max}	Transition	Solvent	Band
	1,3-Butadiene 1,3,5-Hexatriene	217 258	21,000 35,000	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Hexane Hexane	K K
	Vinyl acetylene	219 228	7600 7800	$\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Hexane Hexane	K K
	Acrolein	210 315	11,500 14	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Ethanol Ethanol	K R
	Crotonaldehyde	218 320	18,000 30	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Ethanol Ethanol	K R
	3-Pentene-2-one	224 314	9750 38	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Ethanol Ethanol	K R
 $-C\equiv C-C=O$	1-Hexyn-3-one	214 308	4500 20	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Ethanol Ethanol	K R
 $O=C-C=O$	Glyoxal	195 280	35 3	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Hexane Hexane	K R
HOOC—COOH	Oxalic acid	~185 250	4000 63	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Water Water	K R

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It is known that as the energy of electronic transitions decreases, their probability usually increases and so ε_{max} also increases. Since conjugation lowers the energy required for electronic transitions, it increases the value of λ_{max} and usually that of ε_{max} also. Thus, ethylene shows λ_{max} 171 nm, ε_{max} 15,530 and 1,3-butadiene λ_{max} 217 nm, ε_{max} 21,000. For more examples of various conjugated chromophores, see Table 2.4.

In general, the longer the conjugated system, the higher are the values of λ_{max} and ε_{max}. Thus, a compound with sufficient conjugation absorbs in the visible region (400–800 nm) and becomes colored. For example β-carotene, an orange pigment present in carrots, has eleven carbon-carbon double bonds and absorbs in the visible region (λ_{max} 450 nm, ε_{max} 14×10^4) and is colored (Yadav 2005).

The historical development of theories with respect to the relationship between the color of a dye and its chemical constitution has been thoroughly investigated. As previously stated, during the mid-nineteenth century, since organic chemistry was only at its embryonic stage of development, chemists utilized mostly empirical methods to synthesize dye. Nonetheless in 1867, Graebe and Liebermann proposed that the color of dye molecules was related to unsaturation within the molecules, having observed that reduction destroyed the color of dyes. An early theory of dyes first formulated by O. Witt provided a basis for understanding the relation between color and the structure of molecule. According to this theory, a dye consists of three components: one or more the fused benzene rings attached to the unsaturated groups called as chromophores (e.g., –N=N–, $-NO_2$, –C=O) and basic groups called as auxochromes (e.g., NH_2, OH groups). Both of them are responsible for the color (Iqbal 2008). Witt's theory was expanded by Dilthey and Wizinger in 1927.

They realized that a chromophore is usually an electron-withdrawing group, while an auxochrome is commonly an electron-donating group and the two are linked through a conjugated system. This particular approach can be considered as the starting point of the donor–acceptor chromogen concept. Although Witt's theory applied to anthraquininoid and azo dyes, it was less successful in comparison with the theory proposed by Armstrong and Nietzki regarding triphenylmethane dyes and an alternative quinonoid theory since color was attributable to the presence of quinonoid ring structure. While the following approaches were investigated to link tautomerism with visible and UV light absorption by dyes together the progress in quantum mechanics during the mid-1920s contributed to the development of qualitative approaches to associate color to chemical constitution (Burkinshaw 2016).

In simple terms, it can be considered that the organic dye molecules contained three main components such as chromogen, chromophore and auxochrome.

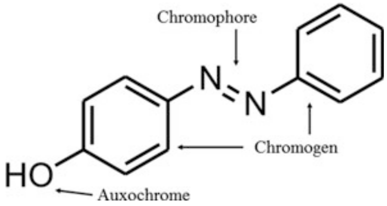
- The chromogen is a chemical compound that is either colored or could be made colored by the attachment of suitable substituent. The chromophore and the auxochrome(s) are also part of the chromogen (Carmen and Daniela 2012).
- The chromophore is a chemical group that is responsible for the appearance of color in compounds (the chromogen) where it is located. The colorants are sometimes also classified according to their main chromophore (e.g., azo dyes contain the chromophore –N=N–) (Iqbal 2008).
- The auxochrome is a substituent group found in a chromogen that influences its color. Whereas, the chromophore or chromophoric group is responsible for chromogen which will be colored. The chromophore itself is not capable of determine a particular color and hue (Marsden 1982). Also, Gurr differentiates two types of auxochrome namely colligators, which are responsible for dye–substrate interactions and which are either ionic (e.g., acidic: $–SO_3^-$, –COOH, etc., or basic: $–N^+$, $–NH_2$) or non-ionic and non-colligators which modify color (Burkinshaw 2016).

The components responsible for color are presented in Schema 2.2 for 4-Hydroxyazobenzene (Solvent Yellow 7).

Unlike most organic compounds, colorants possess color because they:

- absorb light in the visible spectrum (400–700 nm),
- have at least one chromophore (color-bearing group),

Schema 2.2 The components of 4-Hydroxyazobenzene



- have a conjugated system, i.e. a structure with alternating double and single bonds, and
- exhibit resonance of electrons, which is a stabilizing force in organic compounds (Hossain 2014).

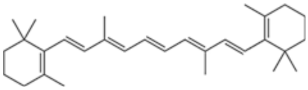
When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (color helpers), examples of which are carboxylic acids, sulfonic acid, amino, and hydroxyl groups (Kumar 2013). While these are not responsible for color, their presence can shift the color of a colorant and they are most often used to influence dye solubility (IARC 2010). Table 2.5 shows the relationships between wavelength of visible and color absorbed/observed. The wavelength spectrum of absorbed light, which determines the color of the matter, is affected by its chemical structure consisting of components such as the chromophores and auxochromes.

Other factors contributing to color are illustrated in Table 2.6 and Schema 2.2. The structures in Table 2.6 demonstrate the importance of having an extended conjugated system. It is evident that doubling the length of the conjugated system in β-carotene and its synthetic homologues causes a significant bathochromic shift, i.e. to a darker color. In addition, resonance also exists across molecules with delocalization of electrical charge among the conjugated atoms and affects the color (Baser and Inanici 1990; Pauling 1939). Consequently there is always more than

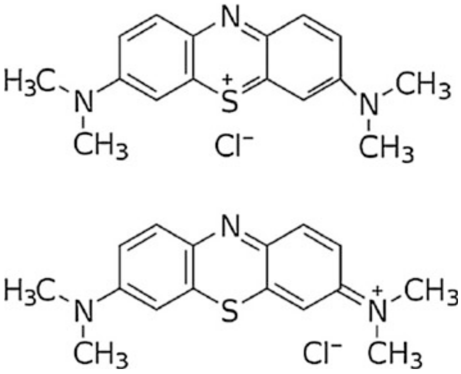
Table 2.5 The relationship between color and wavelength of absorbed light

Wavelength absorbed (nm)	Color absorbed	Color observed
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue-Green	Red
500–560	Green	Purple
560–580	Yellow-Green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-Blue
605–700	Red	Blue-Green

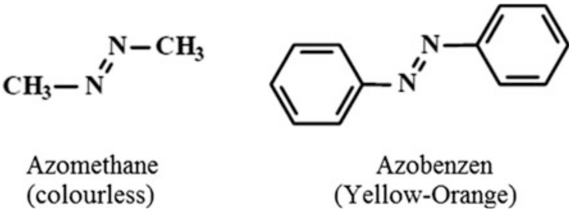
Table 2.6 Conjugation in β-carotene and its synthetic homologues

Carotenes	Double Bond (C=C) Number	Color
 $C_{30}H_{44}$	7	Yellow
$C_{40}H_{56}$ (β-carotene)	11	Red-Orange
$C_{50}H_{68}$	15	Dark blue
$C_{60}H_{80}$	19	Black

Schema 2.3 Different resonance structures of Methylene blue



Schema 2.4 The relation of chromophore group, conjugation and color. Reproduced from IARC, Copyright 2010, with permission from WHO

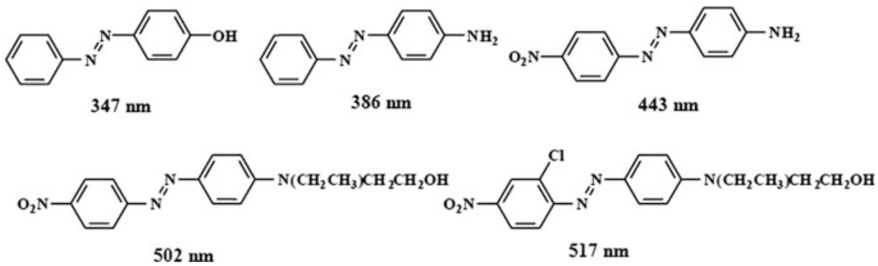


one way to draw the structure of a dye. For example, Methylene blue, commonly used in textile and paper industry is represented by Schema 2.3. The alternating double bonds are all equivalent. The positive charge is shared by the nitrogen and sulfur atoms; in fact it is distributed across the whole cation and not localized at any particular atom (Kiernan 2001).

Regarding the requirement of a chromophore generating color in organic compounds, it is important to note that the chromophore must be part of a conjugated system. This is illustrated through the examples in Schema 2.4 where it can be seen that placement of an azo group between methyl groups produces a colorless compound, while a yellow-orange color is obtained when the azo group is placed between aromatic rings (IARC 2010).

In addition to influencing solubility, auxochromes are essential ring substituents in providing target colors. This is illustrated in Schema 2.5, where the following effects of substituents are shown:

- Adding groups of increasing electron-donating ability to the azobenzene structure has a bathochromic effect (cf. OH vs. NH_2).
- Electron-donating (NH_2) and electron-accepting (NO_2) groups placed in conjugation provide a bathochromic effect. In this regard, nitro groups are especially beneficial, contributing to their prevalence in disperse dye structures.
- Increasing the number of electron-attracting groups conjugated with the electron-donor has a bathochromic effect (Asiri 2001).
- The electron-donating effects of an amino group are enhanced by adding alkyl groups to the N-atom.



Schema 2.5 Effects of substituent groups within an azo-dye system. Reproduced from IARC, Copyright 2010, with permission from WHO

2.4 Light and Color

Visible light is that part of the electromagnetic spectrum, shown in Fig. 2.2, with wavelengths between the red limit at about 700 nm and the violet limit of 400 nm. Depending on the observer, light intensity, etc, typical values for the spectral colors are red, 650 nm; orange, 600; yellow, 580; green, 550 and 500; and blue, 450 (Chittka and Waser 1997).

Color is the part of perception that is carried to the eye from our surroundings by differences in the wavelengths of light (Edge 2003). First, this involves the nature and spectral power distribution in the light from the illuminating light sources. Next, there are several often interrelated processes derived from the interaction of the illumination with matter including absorption, reflection, refraction, diffraction, scattering, and fluorescence. Finally, there is the perception system, involving the eye and the transmission system from eye to brain, leading to the final interpretation reached in the brain (Kirk-Othmer 1998c).

Dye chemistry has evolved together with the organic chemistry during the nineteenth century. Initially, the developments about dye have been faster and such developments provided significant contributions also to the development of structural organic chemistry. The structural theory is developed to understand not only the

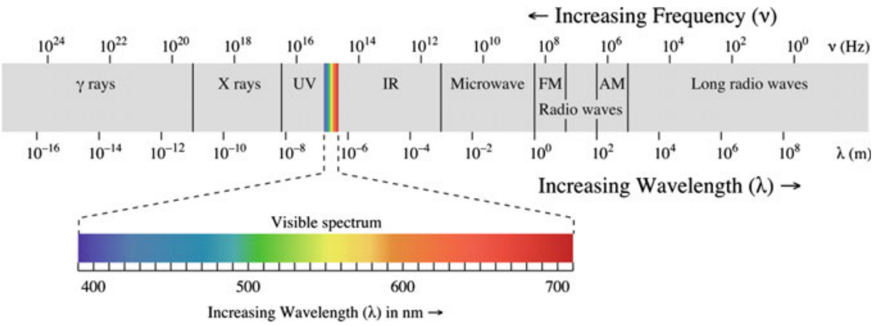


Fig. 2.2 The electromagnetic spectrum

chemistry of dye but also the origins of colors in dyes. This was particularly true for the late nineteenth-early twentieth century period, as the electronic theory of molecular structure began to be developed. Thus it is of interest to review briefly the development of color and constitution theory from the time of the first synthetic dyes, and to see how this has led to a situation where modern computers can now be used to predict the color of a dye before it has even been synthesized. At the time of Perkin's discovery, organic chemistry as a science was still in its infancy. Therefore, the structure of benzenoid compounds could not be properly understood until Kekule's theory in 1865. It should also be considered that the electron was not discovered until 1897 and the concept of the electron-pair bond was formulated by Lewis in 1916 (Shaik 2007). Until 1868, the sufficient data that are associated with the unsaturation in the dye molecules and color about synthetic dyes have accumulated (Akaoui 1976). The first real attempt to interpret the color of dyes in terms of their molecular composition was made by Witt in 1876. By this time, structural chemistry had progressed to a stage where functional groups were well understood, and Witt had imagined a dye molecule formed from three components. Thus, he defined benzene, or fused benzene, rings, and simple unsaturated groups attached to these rings, e.g., $–NO_2$, –N=N–, –C=O as chromophores. He also defined basic groups, e.g., $–NH_2$, –OH, as auxochromes and remarked that the presence of all three units produced intense color. Witt's theory was readily applicable to the azo and anthraquinone dyes, but it could not easily be reconciled with the triphenylmethane cationic dyes. Thus, a complementally alternative interpretation associated with the origin of color was proposed quite independently by the theory proposed by Armstrong and Nietzki. Eventually, it was suggested that color is associated with the presence of quinonoid structures (i.e., benzenoid rings modified to a cyclohexadiene residue with two exocyclic double bonds). For example, these units had to be present in the formulated structures of the cationic dyes. Generally more than one quinonoid structure could be drawn, and it was a logical step to assume that some kind of oscillation of the structure between these possibilities was responsible for light absorption. In fact, the electromagnetic wave theory of light had been accepted for a long time, and the interaction of a vibrating wave with an oscillating bond system provided an attractive mechanism for the absorption process. However, simple theoretical considerations showed that the frequency of atomic vibrations were far too low to be matched with the frequency of light. After the discovery of the electron, it was pointed out that vibrations of such a particle would involve the correct sort of frequency for light absorption, but this suggestion was not treated seriously by chemists at the turn of the century. By Lewis's electronic theory related with the bonding in molecules after significant progresses in theoretical chemistry in the early 1900s, light absorption over electronic excitation was widely accepted.

One important theoretical concept associated with color was mesomerism. In 1899, conjugation and partial valence hypothesis in order to explain the anomalous chemical properties of conjugated polyene systems had been published. Therefore it was suggested that chain termini possess partially unsatisfied valencies in such system. In subsequent years, the concept of "limiting structures" for depicting of the true structure of a molecule had been developed. Such ideas that laid the foundations for mesomerism exposed the concept of “average structure” as the chromostate in recognition of its apparent direct relevance to color. For example, a triphenylmethane dye can be regarded as an average of three limiting structures, and the consequent chromostate is highly colored.

The most important advance in theoretical chemistry was the quantum mechanics whose mathematical formulation was first developed in 1925 with the independent contributions of Schrodinger and Heisenberg. By the early 1930s, quantum mechanics has been applied to the subject of bonding in molecules (for example the π-bond was mathematically formulated in 1930). At this stage, the concept of mesomerism used by the organic chemist, and a new concept called as resonance began to be used as equivalent on the basis of quantum mechanical calculations. The approximation related with this concept is based on the valence bond theory, and it was subsequently used also to calculate the absorption spectra of dyes. Also in the early 1930s, an alternative mathematical approximation that utilizes quantum mechanics to calculate the properties of molecules was developed, namely, molecular orbital theory (Jones 2015). Many of the properties of complex conjugated organic molecules were quantified by using this method referred to as Hückel molecular orbital (HMO) theory.

With the introduction of the valence bond and HMO methods, the applications of these theories in subsequent years contribute a great deal to dyes and the attempts to predict color. For example, in 1939 the application of the HMO method to the absorption spectra of polyenes and cyanine dyes was made with considerable success, and by the same year, valence bond theory was also used in relation with the colors of cationic and anionic dyes. In 1940 the spectroscopic shifts in polyene dyes caused by increasing chain length were calculated, and then the well-known convergent and non convergent vinylene shifts in unsymmetrical and symmetrical cyanine dyes were also determined by using valence bond theory. Thus, it may be said that satisfactory physical interpretations about the structure of organic molecules with the means for calculating the light absorption properties of dyes were established sufficiently until 1940. In 1942, a new quantum mechanical approach to calculate the properties of conjugated organic molecules was introduced. This approach known as the “electron gas” or “free electron” method has been quite successful for calculating the spectroscopic properties of simple dyes, and has been exposed to the many changes in later years. In 1950s, a different form of HMO theory was used to determine the color for many cyanine-type dyes with notable success.

In 1953, the theoretical approaches based on HMO theory that could include electronic interactions were emerged. The new computational procedure as referred to as the Pariser-Parr-Pople (PPP) method has been very successful for calculating the electronic spectra of π-electron systems. Then, by the development of suitable molecular parameters it has been proved to be one of the most successful color prediction techniques for routine use at the present time. One disadvantage of the PPP method is that it ignores σ-electrons and considers the π-electrons only.

Until the 1970s, Various MO procedures were developed and these methods have become as easily applicable to complex dye structures as the PPP method. Although enormous strides in the area of mathematical color prediction have been made, qualitative color and constitution theory still occupy an important place in terms of dye chemistry. As all these approaches have an important place in the context of the modern dye chemistry, they may give an insight about the origins of color in dyes and also general electronic structural theory of organic compounds (Griffiths 1990).

A completely new approach which would not only provide a new insight into color structure relationships but would also allow quantitative assessments to be made was required. The Einstein-Planck quantum theory, which states that energy is not continuous but can only have certain discrete (quantized) values, constituted such a breakthrough. From this new fundamental theory, two modern theories of color and constitution have emerged: Valence Bond (VB) theory and Molecular Orbital (MO) theory. The major difference between the two theories is that the former is based on the concept of bonding valence electron pairs being localized between specific atoms in a molecule, whereas the latter is depend on the pictures of electrons showing distribution among a set of molecular orbitals of discrete energies. On the other hand, Huckel made the major breakthrough using these theories to calculate the various properties of unsaturated molecules. Huckel had made perhaps the most drastic assumption considering σ and π electrons separately. Use of MO (HMO) theory by Huckel provided the calculation of properties of unsaturated molecules (ethylene, butadiene and benzene). In 1948, Kuhn developed the Free Electron MO (FEMO) model, which is the simplest of the MO models. It is suitable only for conjugated systems in which all the bonds have similar n-bond order such as the cyanine dyes. The first general MO theory for dyes was proposed by Dewar in 1950. A set of rules for predicting qualitatively the effect of substituent on the color of a dye was formulated by using MO (PMO) theory. In 1951, the many equations based on LCAO-MO theory was developed by Roothaan to describe the behavior of molecules. If these equations could be solved for dye molecules, it would enable to calculate precisely both the color and the tinctorial strength. However, they are theoretical in nature and unsuitable for tackling the complex molecules of organic chemistry. Consequently, Pariser, Parr and Pople designed a semi-empirical theory to predict the wavelengths and intensities of the main visible and ultra-violet bands of unsaturated organic molecules by using Roothaan equations in 1953. The Pariser-Parr-Pople (PPP) model incorporated the n-electron by considering only the assumption of Huckel plus a self-consistent-field (SCF) treatment to take account of electron-electron interactions. It also considers the configuration interaction (CI) treatment to include the effect of other transitions on the main highest occupied to lowest unoccupied MO (HOMO → LUMO) transition. Both these treatments provide to obtain a better (more real) solution. In addition, more complex integrals in the equations were neglected whilst values for others were obtained from experimental data.

PPP model was used widely and successfully for predicting the color and tinctorial strength of dyestuffs especially for azo dyes (Gordon and Gregory 1987).

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Chapter 3
Classification of Dye and Pigments

Abstract The global market for pigments and dyes is forecast to reach 9.9 million tons and $26.53 billion by the year 2017, driven by the growth in key end-use industries. Before synthetic dyes and pigments were discovered, limited number of natural colorant has been obtained from plants, animals and minerals. The classification of colorants has become mandatory due to huge increase in kind and number of colorants. For this reason, colorants are classified based on their structure, source, color, solubility and application methods. In this chapter, dyes will be investigated in two different groups as accordance with chemical structures and application methods. The basic classification groups were determined as azo, anthraquinone, indigo, phthalocyanine, sulfur, nitro and nitroso dyes by considering their chemical structures. According to application method, they were grouped as reactive, disperse, acid, basic, direct, and vat dyes. However, the classification of pigments as organic and inorganic pigments is also regarded as an appropriate way.

Keywords Dye · Pigment · Classification · Chemical structure · Indigo · Anthraquinone · Phthalocyanine and azo dyes · Sulfur · Nitro and nitroso dyes · Application method

3.1 Introduction

Dyes and pigments have an extensive range of applications such as textiles, paper, paints, coatings, plastics, construction, cosmetics, food, glass, automotive, and printing inks. Global colorant market is expected to drive due to increased coloring needs of various end use industries ranging from textiles to coatings. In addition, rising demand for high performance colorants and increased consumer preference towards eco-friendly products is expected to further propel global industry demand over the forecast period (Grand View Research 2015). The global market for pigments and dyes is forecast to reach 9.9 million tons and $26.53 billion by the year 2017, driven by the growth in key end-use industries (Paint & Coating Industries 2015).

A. Gürses et al., *Dyes and Pigments*, SpringerBriefs in Green Chemistry
for Sustainability, DOI 10.1007/978-3-319-33892-7_3

Table 3.1 The main colorant categories and color index constitution numbers

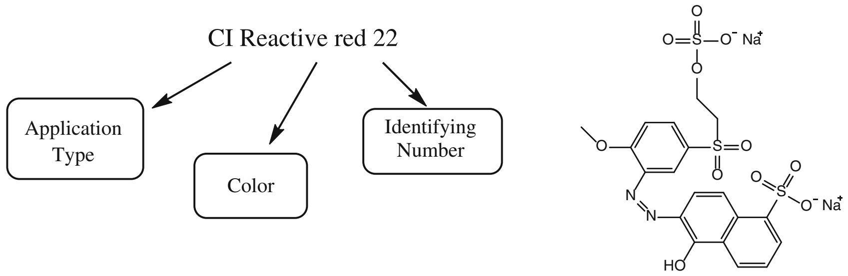
Range	Chemical structure	Range	Chemical structure
10000–10299	Nitroso	49400–49699	Indamine
10300–10999	Nitro	49700–49999	Indophenol
11000–19999	Monozo	50000–50999	Azine
20000–29999	Disazo	51000–51999	Oxazine
30000–34999	Trisazo	52000–52999	Thiazine
35000–36999	Polyazo	53000–54999	Sulfur
37000–39999	Azoic	55000–55999	Lactone
40000–40799	Stilbene	56000–56999	Aminoketone
40800–40999	Carotenoid	57000–57999	Hydroxyketone
41000–41999	Diphenylmethane	58000–72999	Anthraquinone
42000–44999	Triarylmethane	73000–73999	Indigoid
45000–45999	Xanthene	74000–74999	Phthalocyanine
46000–46999	Acridine	75000–75999	Natural
47000–47999	Quinioline	76000–76999	Oxidation bases
48000–48999	Methine	77000–77999	Inorganic pigments
49000–49399	Thiazole		

Before synthetic dyes and pigments were discovered, limited number of natural colorant has been obtained from plants, animals and minerals. The classification of colorants has become mandatory due to huge increase in kind and number of colorants. For this reason, colorants are classified based on their structure, source, color, solubility and application methods. However, due to the complexities of the color nomenclature based on the chemical structure, the classification based on application is often considered as more advantageous (Yagub et al. 2014; Rauf et al. 2011; Abdullah 2010).

Dye classification on the basis of the use or application is the principal method adopted by the Color Index (C.I.) (Pepling et al. 1997). According to Color index classification, each colorant is assigned a C.I., consisting of generic name and a chemical constitution number (Table 3.1) (Tapley and Fan 2005). Generic name contains application type, color or hue and identifying number. A five digit C.I. number is assigned to a dye when its chemical structure has been disclosed by the manufacturer (Gupta and Suhas 2009).

Reactive red 22, which is a member of mono azo dyes, has been given as a representative example to illustrate the color index classification (Schema 3.1).

The formal chemical names of most dyes are so long that they are never used in ordinary conversation or writing (for example, the IUPAC name of Malachite green (C.I. Basic green 4) is 4-{[4-(dimethylamino) phenyl] (phenyl) methylidene}-*N*, *N*-dimethylcyclohexa-2.5-dien-1-iminium chloride) (Kumar et al. 2014). Instead, each dye has one or more informal names. Most informal names include the color, and some also indicate a major property or the general class of compounds to which the dye belongs. Names may commemorate scientists (e.g., Bernthsen's methylene



Chemical Name	: Sodium (Z)-2-((3-((1-hydroxy-5-sulfonatonaphthalen-2-yl) diazenyl)-4-methoxyphenyl)sulfonyl) ethylsulfate
Molecular formula	: $C_{19}H_{16}N_2Na_2O_{11}S_3$
Molar mass	: 590,50
C.I. number	: 14824
CAS number	: 19526-81-9
Application class	: Reactive
Commercial names	: Remazol Red B, Celmazol Red B, Diamira Red B, Sumifix Red B

Schema 3.1 The representative example for the color index classification

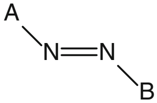
violet, Bindschedler's green, Meldola's blue), or include a former or current manufacturer's name or trade-names (Hoechst 33258, Sirius red F3B, Procion brilliant red M2B) (Fay 1911). The informal name of a dye commonly includes a suffix of one or more capital letters and sometimes also one or more numbers. Frequently the suffix distinguishes the compound from similarly named products of the same manufacturer, or it may be part of a nonproprietary name. However, many dyes have standardized CI names based on their original industrial uses and colors (Kiernan 2001).

Dyes can be investigated in two different groups as accordance with chemical structures and application methods.

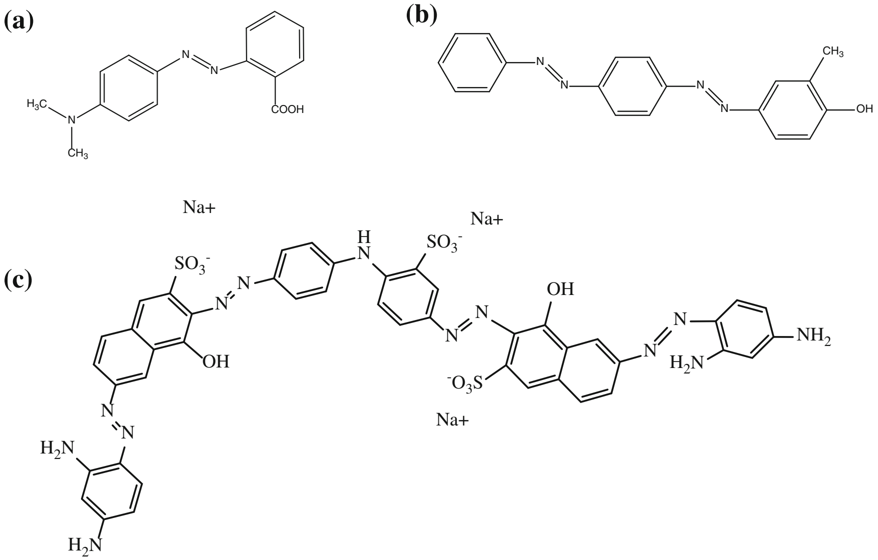
3.2 Dye Classes According to Chemical Structures

3.2.1 Azo Dyes

Azo dyes are the most widely used dyes and represent over 60 % of the total dyes (Gupta and Suhas 2009; Shah 2014). Azo dyes contain at least one nitrogen-nitrogen (N=N) double bond, however many different structures are possible (Growther and Meenakshi 2008). The azo group is attached to two groups of which at least one but, more usually, both are aromatic (Schema 3.2).



Schema 3.2 Example of an azo group attached to two different groups



Schema 3.3 Various azo dyes examples. **a** Acid red 2, **b** Disperse yellow 7 and **c** Direct black 22

They exist in the *trans* form in which the bond angle is ca. 120°, the nitrogen atoms are sp^2 hybridized. In monoazo dyes, the most important type, the A group often contains electron-accepting substituents, and the B group contains electron-donating substituents, particularly hydroxyl and amino groups. If the dyes contain only aromatic groups, such as benzene and naphthalene, they are known as carbocyclic azo dyes. If they contain one or more heterocyclic groups, the dyes are known as heterocyclic azo dyes (Gregory 1990; Julkapli et al. 2014). The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes (Rauf et al. 2011). Examples of various azo dyes are presented in Schema 3.3.

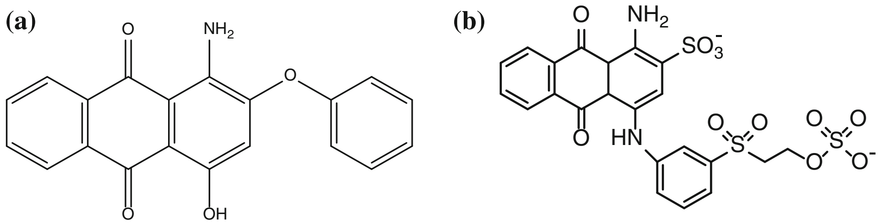
Azo dyes are, due to their relative simple synthesis and almost unlimited numbers of substituents, most important group of synthetic colorants that are extensively used in textile, pharmaceutical, plastic, leather, paper, and printing industries and they do not occur naturally (Øllgaard et al. 1998; Puvaneswari et al. 2006). Almost without exception, azo dyes are made by diazotization of a primary aromatic amine followed by coupling of the resultant diazonium salt with an electron-rich nucleophile (Hunger 2003).

3.2.2 Anthraquinone Dyes

Anthraquinone dyes are the second most important class after azo dyes (Saranraj 2013). They are also one of the oldest types of dyes since they have been found in the wrappings of mummies dating back over 4000 years. The anthraquinone dyes have important advantages such as brightness and good fastness properties (Gregory 1990). In contrast to the azo dyes, which have no natural counterparts, anthraquinones are important natural products found in bacteria, fungi, lichens and plants (Han et al. 2001). Most of anthraquinone dyes have high molar extinction coefficients and strong absorption bands in long-wavelength region. The photo stability of anthraquinone dyes is also excellent at least from their textile dyeing application. Therefore, anthraquinone dyes has been used for application in dye-sensitized solar cells (Li et al. 2007). The more complicated syntheses and lower tinctorial strengths of the anthraquinone dyes make production costs higher than for azo dyes (Bien et al. 2011).

The anthraquinone structure is the basic building block of these dyes and other derivatives can be built around the anthraquinone structure. There can be many substitutions, including junctions with other fused ring systems. This is by far the largest group of carbonyl dyes including hundreds of compounds that are applied to textiles in many ways. The most notable from an industrial standpoint are the anthraquinone vat dyes for cotton; disperse dyes and pigments (Kiernan 2001). Two examples of anthraquinone dyes are presented in Schema 3.4.

The production of anthraquinone intermediates and anthraquinone dyes generally proceeds from a few key products generated by electrophilic substitution of unsubstituted anthraquinone or by synthesis of the nucleus. The major methods employed to prepare anthraquinone derivatives substituted in the α position are sulfonation and nitration. Preparation of β-substituted anthraquinones and of quinizarin (1,4-dihydroxyanthraquinone) generally is accomplished by synthesis of the nucleus starting from phthalic anhydride and a benzene derivative (Bien et al. 2011).

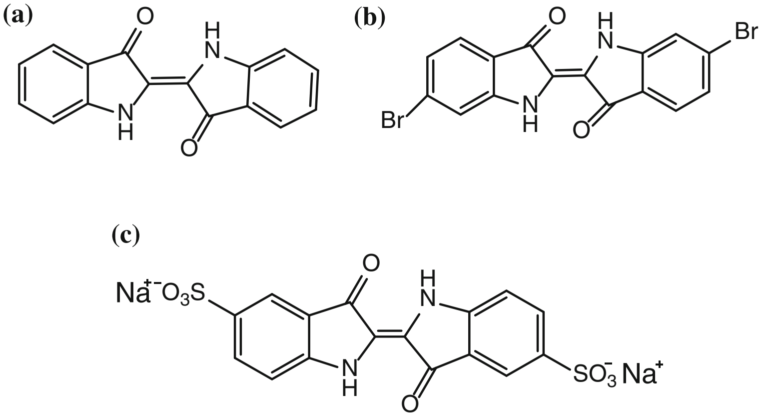


Schema 3.4 Typical two examples for anthraquinone dyes. **a** Disperse red 60 and **b** Reactive blue 19

3.2.3 Indigoid Dyes

Indigo dye is an organic compound with a distinctive blue color and represents one of the oldest organic dyes known. Indigo dye which is firstly extracted from plants has been used for textile dyeing for 5000 years (Hunger 2003). Indigo is used almost exclusively for dyeing denim jeans and jackets (Ünlü 2008). It is held in high esteem by the young who like its blue color and the fact that it fades on tone to give progressively paler blue shades. Although many indigoid dyes have been synthesized, only indigo (Schema 3.4a) is of any major importance today (Gregory 1990). The synthesis of other indigoid compounds is also important in medicine, semiconductor, and cosmetics alongside the textile products. Schema 3.5 shows the chemical structures of indigo and other two indigoid dyes.

Until the late 19th century, indigo was obtained from natural sources and, with the advent of the modern chemical industry, became one of the first natural molecules to be synthesized. Synthetically-produced indigo was of superior quality to indigo from plants, and was therefore preferred by dyers.Today, almost all the traded indigo is produced synthetically and, in general, the branded industrial production is based on variations of the Pflegers's method (Głowacki et al. 2012). In the largely used process, the synthesis involves the reaction of aniline, formaldehyde and hydrogen cyanide, affording phenylglycinonitrile that is then hydrolyzed to N-phenylglycine. Subsequently, the N-phenylglycine is treated with molten mixtures of caustic soda and sodamide at 200 °C to afford indoxyl, which undergoes further oxidative dimerization to form indigo (Rebelo et al. 2014).

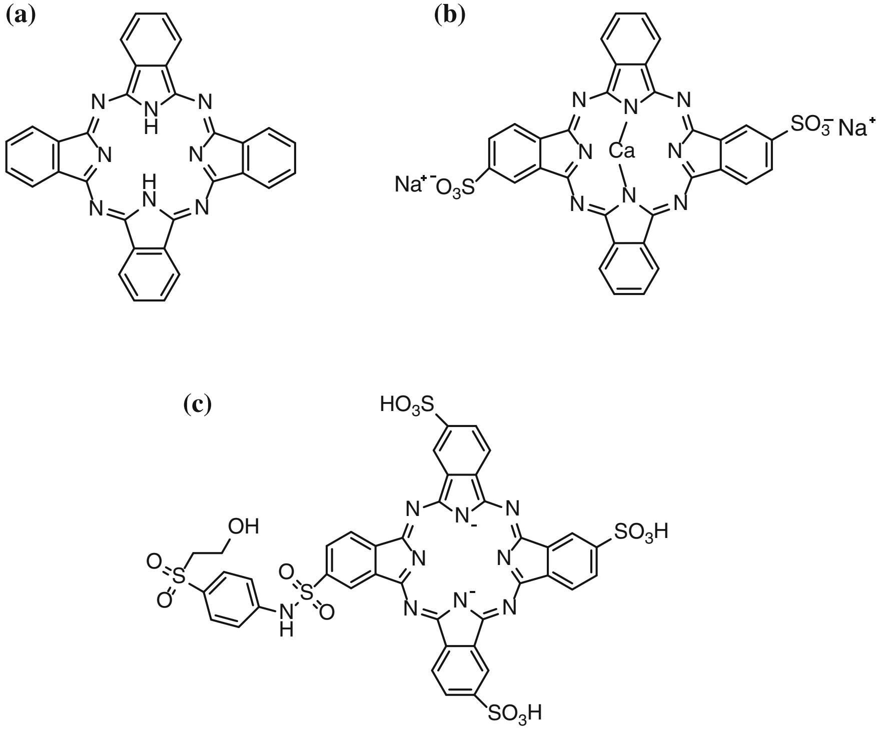


Schema 3.5 The chemical structures of indigoid dyes. **a** Indigo, **b** Tyrian purple and **c** Indigo carmine

3.2.4 Phthalocyanine Dyes

Phthalocyanines are a class of macrocyclic compounds possessing a highly conjugated π-electron system, intense absorption in the near-IR region (Durmuş and Nyokong 2008). Phthalocyanines display a number of unique properties, such as increased stability, architectural flexibility, diverse coordination properties, and improved spectroscopic characteristics, which make them of great interest in various scientific and technological areas (Sahin et al. 2015). The combination of aromaticity in an extended π-system including four fused benzenoid aromatics is essential not only for intense color in the visible range of 650–750 nm but also especially in the solid state for an excellent thermal and chemical stability of mostly planar phthalocyanines (Wöhrle et al. 2012).

Phthalocyanine forms coordination complexes with most elements especially metals such as Cu, Fe, Si, Ge, and As. These intensely colored complexes with various elements are used in dyes and pigments (Hunger 2003). The chemical structures of phthalocyanine and its some complexes are represented in Schema 3.6.



Schema 3.6 The chemical structures of phthalocyanine (**a**) and its some derivative dyes; Direct blue 86 (**b**), Reactive blue 21 (**c**)

Phthalocyanines are usually prepared by the high temperature cyclotetramerization processes of either phthalonitrile or phthalic anhydride, in which the template effect afforded by a suitable metal cation is required. The reactions can be carried out in a variety of solvents as well as under solvent-free conditions both processes require high temperature ca. 200 °C and long reaction times (Kantar et al. 2015).

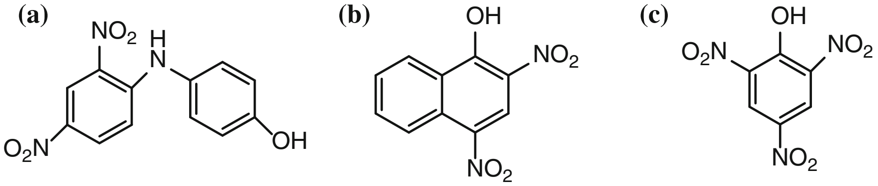
Phthalocyanines are analogs of the natural pigments. However, unlike these natural pigments, which have extremely poor stability, phthalocyanines have exceptional stability and are probably the most stable of all the colorants in use today. Substituents have only a minor effect on the color of phthalocyanines and so their hues are restricted to blue and green (Nemykin and Lukyanets 2010). As well as being extremely stable, phthalocyanines are bright and tinctorially strong; this renders them cost effective (Gregory 1990). It is reported that the phthalocyanines have interesting optoelectronic properties and they have been used in many new applications such as liquid crystals, optical and electronic devices, chemical sensors, non-linear optics, and fibrous assemblies beside printing inks and paints due to their (Thimiopoulos et al. 2014).

3.2.5 Sulfur Dyes

With a few exceptions, sulfur dyes are used for dyeing cellulosic fibers. They are insoluble in water and are reduced to the water-soluble leuco form for application to the substrate by using sodium sulfide solution. The sulfur dye proper is then formed within the fiber pores by atmospheric or chemical oxidation. Sulfur dyes constitute an important class of dye for producing cost-effective tertiary shades, especially black, on cellulosic fibers. One of the most important dyes is C.I. Sulphur Black 1, prepared by heating 2,4-dinitrophenol with sodium polysulfide (Hunger 2003).

Sulfur dyes are synthesized by heating aromatic amines, phenols, or nitro compounds with sulfur or, more usually, alkali polysulfides (Khandal 2006). Unlike most other dye types, it is not easy to define a chromogen for the sulfur dyes. It is likely that they consist of macromolecular structures of the phenothiazonethianthrone type, in which the sulfur is present as (sulfide) bridging links and as thiazine groups (Gregory 1990).

Sulphur dyes possess neither well defined chemical structures nor consistent in composition; are just specified with raw material and process used to manufacture. Indeed, excess sulphur is isolated from dye after synthesis. Sulphur linkages are the integral part of chromophore and are basically complex mixture of polymeric molecular species comprising of large proportion of sulphur in the form of sulphide (–S–), disulphide (–S–S–) and polysulphide (–Sn–) links in heterocyclic rings. Chromophoric systems are based on thiazole, thiazone, thianthrenes and phenothiazonethioanthrone. Synthesis of sulphur dyes, in general, involves sulphurisation, in which sulphur, polysulphide or both in mixture is heated at around 180–350 °C along with aromatic amines, phenols or aminophenols or refluxed in solvents under



Schema 3.7 The chemical structures of nitro dyes: **a** Disperse yellow 1, **b** Acid yellow 24 and **c** Picric acid

pressure. Sulphurised vat dyes are synthesized in the same way too but their reduction requires a strong reducing agent like sodium hydrosulphide (Chakraborty 2010).

Sulfur dyes are mainly used for dyeing textile cellulosic materials or blends of cellulosic fibers with synthetic fibers, but they also find specific applications in the dyeing of silk and paper in limited quantities and use on certain types of leathers. Amongst synthetic dyes, sulfur dyes have the dullest range of colors of all dyestuff classes, are inexpensive and exhibit excellent washing and good light fastness. These properties, along with the ease of application, ensure that the consumption of sulfur dyes remains high (Nguyen and Juang 2013).

3.2.6 Nitro and Nitroso Dyes

These dyes are now of only minor commercial importance but are of interest for their small molecular structures. The early nitro dyes were acid dyes used for dyeing the natural animal fibers such as wool and silk (Gregory 1990). The chemical structures of some nitro dyes are shown in Schema 3.7.

These dyes have one or more nitro or nitroso group conjugated with an electron donating group via an aromatic system. Hydroxynitroso compounds are formed by the action of nitrous acid on phenols and naphthols. The nitroso compounds have not themselves dyeing properties, but are capable of forming metal complexes that are either pigments or, if the starting compound bears hydrophilic groups, are acid dyes.

3.3 Dye Classes According to Application Methods

3.3.1 Reactive Dyes

Reactive dyes differ from other class of dyes in that their molecules contain one or more reactive groups capable of forming a covalent bond with a compatible fiber group. They have become very popular due to their high wet-fastness, brilliance and range of hues (Pereira and Alves 2012). These dyes consequently have a reactive group that enables them to react with the hydroxy group of the cellulose. The reactive group is normally attached to the chromophore via a bridging group such as –NH–, –CO–, and SO_2–. As for direct dyes, solubility is usually guaranteed by attaching at least one sulphonic acid group to the molecule. According to their application technique, the reactive dyes can be classified as alkali-controllable, salt-controllable and temperature-controllable dyes (Başer and Inanici 1990; Ferus-Comelo 2002).

3.3.2 Disperse Dyes

Disperse dyes generally contain azo, anthraquinone, nitro groups and they are substantially water-insoluble dyes having substantivity for one or more hydrophobic fibers such as nylon, cellulose, cellulose acetate, and acrylic fibers with usually applied from fine aqueous dispersion (Burkinshaw 2016; Gupta and Suhas 2009). Dyeing is usually followed by a reduction-clear to prevent staining from the unfixed dye. During the dyeing process, the dye molecules in solution are attached to the fibers and then dispersed dye molecules transfers to solution despite to their low solubility. Thermal transfer printing and dye diffusion thermal transfer processes for electronic photography represent rich markets for selected members of this class (Ejder-Korucu et al. 2015).

3.3.3 Acid Dyes

Acid dyes are organic sulfonic acids; the commercially available forms are usually sodium salts, which exhibit good water solubility. In sequence of their importance, acid dyes are mostly used with certain fiber types such as polyamide, wool, silk, modified acrylic, and polypropylene fibers as well as blends of the mentioned fibers with other fibers such as cotton, rayon, and polyester, regular acrylic (Ayad and El-Nasr 2012). Their colors are generally bright and fastness to light and washing range from poor to excellent, depending on the chemical structure of the dyestuff. The most acid dyes are sulfonic acid salts and they contain azo, anthraquinone, triphenylmethane, nitro and nitroso chromophoric groups.

3.3.4 Basic Dyes

Basic dyes known as cationic dyes have positive charge generally resulting from the ammonium cation. These water-soluble cationic dyes are applied to paper, polyacrylonitrile, modified nylons, and modified polyesters. Their original use was for silk, wool, and tannin-mordanted cotton when brightness of shade was more important than fastness to light and washing. Basic dyes are water-soluble and yield colored cations in solution (Hunger 2003). Generally, these dyes are not applied along with acid or direct dyes because precipitation may occur. On most fibers, basic dyes have low colorfastness. However, on acrylic fibers, cationic dyes exhibit relatively good colorfastness resulting from some covalent bonding. Basic or cationic dyes derive their name from the fact that the dye molecules dissociate in water, with the cation being the colored portion of the dye. If anionic sites are present in the fiber, the dye will be attracted to form a covalent bond. Because anionic sites vary in terms of availability with various fibers, the durability of cationic dyes is quite variable (Considine 1995).

3.3.5 Direct Dyes

Direct dyes are water-soluble dyes, easily applied to cellulose fibers, and comprise the largest group of dyes (Considine 1995). They have been defined as anionic dyes with substantivity for cellulosic fibers which are normally applied from an aqueous dye bath containing an electrolyte. Direct dyes do not require the use of a mordant and, as their name implies, the dyeing procedure is quite simple. The goods go into the bath followed by the dissolved dyes. The bath is then gradually heated, usually to the boil, and additions of salt promote dyeing (Broadbent 2001). In addition they have higher exhaustion rate, with lower electrolyte requirement compared to reactive dyes. Both contribute to a better environmental performance. Most of the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines, and oxazines (Hunger 2003). Compared to other dye classes, direct dyes have a high molecular mass which, as a general rule, promotes dye aggregation and substantivity to the fiber. Water solubility is usually conferred by sulphonation. Interestingly, the high substantivity of many direct dyes not only leads to higher exhaustion values, and consequently to good color reproducibility, but also to higher adsorption ratios on the activated sludge of wastewater treatment plants. High substantivity may therefore result in a double environmental benefit (Ferus-Comelo 2002).

3.3.6 Vat Dyes

Indigo is one of the known oldest dyes and it is a natural vat dye has been used for nearly 4000 years. Vat dyes are water-insoluble pigments. They are called dyes because chemical reduction in alkaline solution converts the pigment into a water-soluble leuco form with substantivity for cotton (Broadbent 2001). Vat dyes are colorfast to laundering and have good fastness to light. These dyes are held to cellulose molecules by van der Waals forces and hydrogen bonding (Considine 1995). Once the reduced dye has diffused into the fiber, it is oxidized and becomes water insoluble again. The water insolubility of the vat pigment in the fiber leads to outstanding wash fastness. Their generally speaking, very good fastness against other environmental impacts such as light or chlorine bleach makes them the dye class of choice for demanding applications despite their high cost. Nevertheless, total processing cost is often lower than in the case of reactive dyes. The decline of their usage may be due in part to their fairly complex application process and a corresponding lack of know-how in many textile dye houses. Most vat dyes are indigoid or anthraquinone and usually have between five and ten aromatic rings. Their main feature is the oxygen atom that is double-bonded to a carbon atom. Under strong alkaline conditions, the oxygen is reduced and the water-soluble leuco vat ion is formed. Otherwise, vat dyes normally contain very few substituents (Ferus-Comelo 2002).

3.4 Inorganic and Organic Pigments

Pigments are inorganic or organic, colored, white or black materials which are practically insoluble in the medium in which they are incorporated. In many cases the general chemical structure of dyes and pigments is the same or very similar. However, the insolubility of pigments can be obtained by avoiding soluble groups in the molecule or by forming insoluble structures (Herbst and Hunger 2004).

Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble in, and essentially physically and chemically unaffected by, the vehicle or medium in which they are incorporated. They alter appearance either by selective absorption and/or scattering of light. Pigments are usually dispersed in vehicles or substrates for application, as for instance in the manufacture of inks, paints, plastics, or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process (CPMA 1993; Aspland 1993).

Pigments can be characterized by their chemical composition, and by their optical or technical properties. The classification of pigments as organic and inorganic pigments is a convenient way. World production of pigments in 2005 was ca. 7.4×10^6 t. Inorganic pigments accounted for ca. 97 % of this (Völz et al. 2011). The organic and inorganic pigments were classified by chemical and/or physical properties in Figs. 3.1 and 3.2, respectively.

The most consumed inorganic pigments in the world according to market breakdown in 2009 are titanium dioxide (62 %), carbon black pigments (10 %), iron oxides (13 %), and chromates (11 %) (Rothon 2012). With few exceptions, inorganic pigments are oxides, sulfides, oxide hydroxides, silicates, sulfates, or carbonates, and normally consist of single-component particles with well-defined crystal structures (Völz et al. 2011).

The most important white pigment is titanium dioxide. The other whites are zinc oxide, zinc sulfate, lithopone, and lead white pigments. Black pigments are carbon black. Colored pigments are bismuth vanadate, chromium (III) pigments,

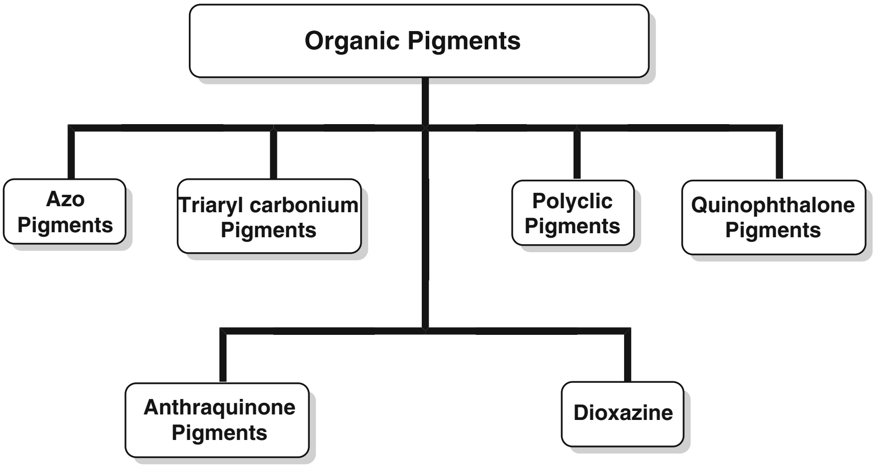


Fig. 3.1 The classification of organic pigments

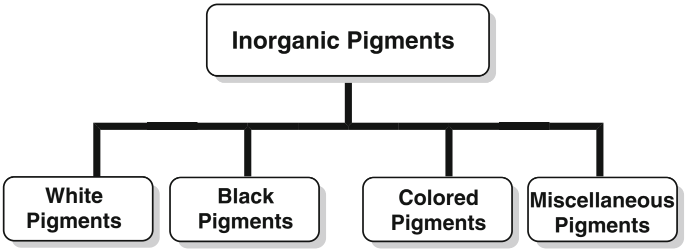


Fig. 3.2 The classification of inorganic pigments

ultramarine pigments, cyanide iron blues, cadmium pigments, lead chromate, iron oxide, and complex inorganic pigments which are mixed metal oxides such as spinels, retiles, and zircon pigments. Miscellaneous pigments can be classified as metal effect pigments, nacreous pigments, transparent pigments, and luminescent pigments (Novotny et al. 1998).

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Chapter 4
Dyeing and Dyeing Technology

Abstract Dyeing is described as the creating of a new and permanent color, by impregnation of especially a dye onto any material namely, textiles, paper or leather. Cochineal, madder, alkanna, henna, brazilwood, red sandalwood, safflower, indigo and logwood were used for the dyeings which can be carried out directly or after mordanting. The goal of dyeing is to provide a uniform coloration for all of fibers forming the material as matched with a pre-specified color. Dyeing is mainly carried out as the continuous or batch processes. Modern dyeing technology consists of several steps determined according to the nature of the fiber and properties of the dyes and pigments for use in fabrics. Other topics which are decisive in terms of the selection of dyeing method or techniques also, cover chemical structure, classification, commercial availability, the fixing properties compatible with the target material, and economic considerations. Many factors can influence the final color. These include fiber characteristics such as the luster, denier, staple length, texture, and cross-section as well as the cloth construction. The dyeing is achieved by the direct application of dye solution onto textiles; whereas, the printing dyeing can be carried out using different specialized techniques. Resist techniques have been in existence in the commercial sector for a long time, with so many different styles and new methods of resist. On the other hand, painting is the practice of application of paint, pigment, color or other medium to a surface and also it is a mode of creative expression. This chapter discuses a wide range of dyeing methods and techniques.

Keywords Continuous and batch dyeing processes · Mordanting · Direct dyeing · Reactive dyeing · Resist dyeing · Ring dyeing · Tie dyeing · Paint · Painting

4.1 Introduction

The dye molecules possess much more complex structures with respect to most common organic compounds' structures. Most of dye molecules contain many conjugated aromatic rings, such as those of benzene or naphthalene. This means the

A. Gürses et al., *Dyes and Pigments*, SpringerBriefs in Green Chemistry
for Sustainability, DOI 10.1007/978-3-319-33892-7_4

presence of a long sequence formed by the alternating single and double bonds between the carbon and other atoms (Shamey and Zhao 2014). This type arrangement often forms the units called the chromophore or color-donating group in the molecule (Abel 1999). Conjugated oligomers of different type, length and degree of substitution behave as tunable systems, with properties strongly facilitating electron delocalization. The smaller energy gap between occupied and unoccupied π-orbitals compared with that between σ-orbitals, leads to absorption and emission of visible light (Limacher 2010; Salzner 2014). Colored compound must contain at least five or six conjugated double bonds in its molecular structure (Sklar 1937).

Water soluble dyes usually have an ionic center in their molecules. This may be the result of a sulphonate group attached to a benzene ring. If the atom bearing the ionic charge is part of a conjugated chain, a delocalized charge as that in a cationic triphenylmethane dye may emerge. Disperse dyes are often substituted azo, anthraquinone or diphenylamine compounds which are non-ionic and don’t contain water soluble groups (Koh 2011). The vat dyes are not soluble in water and so they are converted to a water soluble leuco form by reduction before dyeing and are re-oxidized to the insoluble pigment form after dyeing the cotton (Neenaz 2015; Zollinger 2003). Commercial dyes may commonly be in the forms of fine powder or granular (Chudgar 2000). However, vat and disperse dyes are available also as aqueous pastes (Aspland 1992). Dyes are also available as liquid solutions or dispersions. These dyes are ideal for continuous dyeing, where simple dilution of the liquid dye allows the rapid preparation of large volumes of dye solutions. Liquid dyes should be stable to heating and cooling, resistant to sedimentation and stratification, and not contain unsafe co-solvents or additives. Commercial dye powders also contain various other chemicals besides the principal dyestuff. The other chemicals are consisted of diluents (salt or starch), wetting agents, dispersants, residual intermediates, anti-dusting agents (oils), buffers (sodium carbonate or phosphates), stabilizers and shading dyes (Ciullo 1996).

In the manufacture of successive batches of a given dye, it is almost impossible to obtain identical products because of slight process variations (Broadbent 2001). The dye powders do not generally consist of a single principal colored chemical. On the contrary, some products may be mixtures of different isomeric colorants and also contain the substantial amounts of the colored by-products from the dye-forming reactions. Many dye powders may be a certain mixture of different pre-dyes, whereas some of them are prepared from mixtures of intermediate. In some cases, the manufactured product (e.g., as for the sulphur dyes) may possess an unknown chemical constitution or be a complex mixture of colored chemicals.

Commercial products are utilized directly for dyeing, but occasionally there may be a need for purified dyes in the dyeing. Although the dye purification is not an easy process, e.g., some additives could be removed by washing of water-insoluble dyes with hot water. The product is then dried and re-crystallized from an appropriate solvent. Finally, the product is ground finely by using a dispersing agent for easy dispersion in water. Water soluble basic dyes are commonly considered as the most difficult to eliminate (Julkapli et al. 2014). For example, if the dye is not too soluble, sulphonated dyes might be salted out several times with sodium acetate, which can be removed after drying by extraction with ethanol. Ion exchange and chromatographic methods may also be sometimes useful. Moreover, the yield of purified dye is always very low and it is often difficult to obtain it if the dye was pure and free from contaminants.

Dye is selected according to several criteria in terms of desired performance, manufacturing restrictions and the costs. Every dye has unique colorfastness properties. Some dyes are known with their excellent wash fastness characteristics while others are famous with their light fastness properties. Dye structure and amount and its bonding to the fabric determine the performance characteristics of dye. Dye combinations in a specific formulation must also be evaluated for their effect on colorfastness (Thiagarajan 2014). Many colors in both the processes of dyeing and painting are obtained by mixing suitable amounts of red, yellow and blue colorants. However, in the process of dyeing; the dyes selected for dyeing a high quality cotton material must be quite different from those for a cellulose acetate fabric. While high washing and moderate light fastness are essential for the first case, these are insignificant for the other case. The colored layer, which is the basic building element of painting, is a mixture of the materials such as pigments and binding media, determining the color quality. The main aspects (color stability and hiding power) of this quality can be of strongly time dependent due to the interactions between the chemical species within the mixture and the surroundings (Hradil et al. 2003).

The goal of dyeing is to provide a uniform coloration for all of fibers forming the material as matched with a pre-specified color (Wang 2004). Many factors can influence the final color. These include fiber characteristics such as the luster, denier, staple length, texture, and cross-section as well as the cloth construction.

Now, the differences between dye-dyeing and paint-painting terms will be briefly discussed. Paint is any liquid material that can be applied to a substrate which after drying is converted to a thin opaque or transparent well adhering solid film. Paints are mainly used for decorative and/or protective purposes (Gunnarsson 2012). Whereas, a dye can generally be described as a colored substance that has an affinity to the substrate to which it applied (Santhi 2013).

Painting is the practice of application of paint, pigment, color or other medium to a surface and also it is a mode of creative expression. Unlike, dyeing is a process which imparts beauty, artistic and aesthetic qualities to a product by applying various color and their shades onto a fabric or fibrous material. Detailed information about paint and painting will be demonstrated in the following sections.

4.2 Dyeing

Dyeing can be done at any stage of the manufacturing of textile-fiber, yarn, fabric or a finished textile product including garments and apparels but may require whitening pre-treatment (Khan and Islam 2015). The property of color fastness depends on two factors such as selection of proper dye according to the textile material to be dyed and the method for dyeing the fiber, yarn or fabric.

The dyeing theory covering a wide range of subjects mainly in the area of physical chemistry has many qualitative aspects that are useful in explaining practical dyeing. However, the physicochemical measurements related with the processes of dyeing providing quantitative data are not identical with an actual dyeing practice (Valko 1957). Some of the subjects included in dyeing theory are:

(a) the states of dyes left in the solution and on fiber, after dyeing and during dyeing; (b) the rates of dyeing processes and how these are influenced by mass-transfer of dye from the bath solution to the dye/fiber interface and by diffusion of the dye from the interface into the fiber; (c) the phenomena occurring at the dye/fiber interface depending on the adsorption of dye molecules and the surface potential; (d) the nature of the interactions between dye and fiber molecules; (e) the thermodynamics of dyeing and (f) the fiber structure and its impact on dyeing rate and equilibrium.

Dyeing theory is extremely significant tool in terms of developing of dyeing technology. However, the results may not match completely with the applications of practical dyeing. The textile dyeing is a complex process occurring in a heterogeneous system, which includes of the auxiliaries like dye enzyme, softener or oxidant (Tzanov et al. 2003). Moreover, dyeing is a reversible process governed by the fundamental laws of thermodynamics and kinetics. The dye adsorption process is generally formed of four main steps: the mass transport of dye to the fiber surface; the mass transfer across the fiber/bulk phase interface; the diffusion of dye molecules into the textile material; and interaction of the dye with the binding sites (Saint-Cyr 1999).

4.3 Dyeing Method and Techniques

The primitive societies had discovered the fact that certain roots, leaves and barks could be usually manipulated in a liquid form, and then used to dye textiles. In addition these techniques were utilized by primitive society to decorate clothing, utensils, and even the body as religious and functional practice. Records date all the way back to over 5000 years ago chronicling the dyeing of fabrics. Excavated cloth fragments that date back to 3000 B.C. evidence the intricate dyeing practices and skills of India as well as hundreds of vibrant colors used to dye things in Peru (Belfer 1972; Goetz 2008). Ancient India was particularly advanced in dyeing techniques and has been known since the sixteenth century for their vibrant colors and designs on fabrics. Resist dyeing techniques probably originated here. Also, Indians discovered the use of mordant to make dyes fast and an integral part of the fabrics, not just a pigment on the surface (Belfer 1972; Goetz 2008).

The dyes derived from natural materials, such as plant leaves, roots, bark, insect secretions and minerals have been the mainly dyes used by human for the coloring of textiles until the discovery of the first synthetic dye in 1856 (Saxena and Raja 2014).

After 1923, the aqueous dispersions of dyes were examined widely and the disperse dyes devoid of ionic soluble groups began to be commonly used instead of ion-amine dyes. For example, the sparingly water-soluble-acetate dyes were applied to cellulose acetate in the form of a fine aqueous dispersion (Burkinshaw 1995). By the development of the fibers such as nylon and acrylic having predominantly hydrophobic nature the use of disperse dyes has also significantly increased. In 1941, after the discovery of highly crystalline and hydrophobic polyester fiber, the researches on the disperse dyes have increased drastically.

Consequently, many new application methods were developed and it generally was also proposed opening up the fiber structure temporarily to facilitate dye penetration (Fourness 1979; Koh 2011).

Coloration of a textile material can be carried out by the many ways: (a) direct dyeing in which the dye in the aqueous solution is in contact with the material is gradually absorbed into the fibers; (b) the dyeing made by using a soluble precursor of the dye; (c) direct dyeing made via the chemical interactions between the dye and certain groups of fibers; and (d) the dyeing made by adhering of the dye or pigment to the surface of fiber using an appropriate binder. All of these methods except the last, at some stage, require the adsorption of the dye (or an appropriate precursor) from the aqueous solution onto the fibers. Although the process is reversible essentially, irreversible changes such as the precipitation of a pigment and the reaction with the fiber may also occur. Dyeing could be applied as a batch exhaustion process, or a continuous impregnation and fixation process.

In the batch exhaust technique, the entire textile during dyeing is in continuous contact with all the dye liquor, and therefore the fibers gradually absorb the dyes. In order to obtain well-penetrated dyeing, some variables such as the dyeing temperature, pH and the concentration of auxiliary chemical must be carefully controlled. This gains a more critical important during the process, if the initially absorbed dye is unable to migrate from heavily dyed to poorly dyed areas (Islam and Mahmud 2015).

In continuous impregnation technique, the fabric is passed through a small bath containing the dye solution and then, is squeezed out using two rubber-covered rollers to remove the excess solution, and this process is called padding (Tomasino 1992). The dye does not migrate from the point of impregnation except for those diffused into the fibers which was assisted by the pressure rollers. Each small fabric segment is contacted with the dye liquor only once to provide a uniform padding across the fabric width and along its entire length. After padding process, the dyes must diffuse into the fibers, and this step is called fixation. It may be as simple as rolling up the fabric and batching it for several hours or as complex as treating it thermally in a steam or hot air oven.

Other operations are usually performed either before or after the actual dyeing process. Pretreatments made by both continuous and batch processes in the dyeing machine are called as scouring and bleaching. In the scouring process the raw material or substrate contains natural and acquired impurities. These substances are removed from the fabric by hot alkaline detergents or soap solutions. The bleaching process removes natural color and impurities carried over after the scouring (van Veldhuisen 1991). After dyeing, the material is rinsed to remove trapped solution but it may need some additional operations in the dyeing machine.

These last operations may include: (a) washing by using detergent at or near the boiling point to remove any unfixed dye or loosely adhering pigment from the fiber surfaces, which this process is called as soaping; (b) the use of chemicals to improve the fastness properties of the dyeing but this process may often cause a change in shade and also the color-matching problem and (c) the use of the finishing chemicals like softeners.

Modern dyeing technology consists of several steps selected according to the nature of the fiber and properties of the dyes and pigments for use in fabrics, such as chemical structure, classification, commercial availability, fixing properties compatible with the target material to be dyed, economic considerations and many others (Guaratini and Zanoni 2000). Dyeing methods have not changed much over time. Water still is the most fundamental component used to clean dye, apply auxiliary chemicals for the dyeing, and also to rinse the processed fibers or fabrics (Moore and Ausley 2004).

The dyeing process involves three steps (Fig. 4.1):

- ***Preparation***: The natural or synthetic impurities in this step are removed from the fabric prior to dyeing (Lakshmishri et al. 2011). For this; aqueous alkaline substances and detergents or enzymes are used. Many fabrics are subjected to bleaching by using hydrogen peroxide or compounds containing chlorine to remove their natural color and also sometimes, additionally optical brightening agents are used (Chequer et al. 2013).
- ***Dyeing***: This step includes the application of the aqueous solution of the dye to the textile substrates, using mainly, synthetic organic dyes, frequently at elevated temperature and pressures (Moore and Ausley 2004; Reddy et al. 2008). It must be known that there isn't any dye which is capable to dyeing all existing fibers as well as there isn't any fiber which may be dyed using all existing dyes (Alcantara and Daltin 1996). In this stage, the dyes and also the some chemical aids which can be used to get a uniform color depth, as well as the color fastness properties suitable for the end use of the fabric, (surfactants, acids, alkali/bases, electrolytes, carriers, leveling agents, promoting agents, chelating agents, emulsifying oils, the softening agents etc.) are applied to the textile material (Hubbe et al. 2012; Reddy et al. 2008; Moore and Ausley 2004).

  It can be recognized that the process of fiber dyeing occurred in main four stages: first of them is the diffusion of the dye from the dye bath to the fiber surface. Second stage comprises the adsorption of the dye onto the surface of fiber. The diffusion of the dye to the fiber core forms the third stage of the

Fig. 4.1 The stages of dyeing process

process. In this stage, which was much slower than the transport of the dye dissolved into the dye bath, the dye diffuses into the interior of the fiber until uniformly dyed. The penetration of the dye to the fiber requires accessible fiber. The dye penetrates through available micro-pores in the case of hydrophilic fibers. On the contrary, the molecular structure in the case of hydrophobic fiber is not convenient for a continuous water phase and therefore it needs the cavity formation in the fibers in order to make possible the penetration of the dye. In general, the access to the fiber can be improved by temperature control. The penetration of the dye into hydrophobic fibers can occur only above the glass transition temperature (sometimes, above 100 °C). During the diffusion into the micro-pores, an electrostatic charge barrier which develops on the surface of the fiber must be overcome. In some cases, salt in large amounts are added to the dyeing bath, in order to reduce the electrostatic charge on the surface of fiber and even to promote the penetration of the dye (Park et al. 2002).

Fourth stage involves also the fixation of the dye on the fiber. There are known many different mechanisms related with the fixation. The chemical interactions between the dye and fiber (Reactive dyes) to van der Waals interactions between the dye and fiber (Direct dyes) are mechanisms related with the fixation. In addition interaction of hydrogen bonding responsible for the interactions between fiber and dyestuff, dyestuff to dyestuff, water to fiber and water to soluble substances present in the liquor (surfactants) has an important role in terms of the fixation (Schönberger 2003).

- ***Finishing***: The operations made with chemical compounds for improving the quality of the fabric are performed at this stage. Permanent press, water proofing, softening, antistatic protection, soil resistance, stain release and microbial/fungal protection are the typical operations which applied onto fabric in the finishing process (Moore and Ausley 2004; Chequer et al. 2013).

  Dyeing is mainly carried out as the ***continuous*** or ***batch*** processes. The most appropriate process depends on several factors, such as type of material (fiber, yarn, fabric, fabric construction, and garment), the generic type of fiber, size of the dye batch, and quality requirements for the dyed fabric, but the batch processes in dyeing of textile materials are more, commonly used.
- ***Continuous dyeing process***: This is the most suitable dyeing process for woven fabrics. Most of continuous processes are designed for dyeing of blends of polyester and cotton (Perkins 1995). In the continuous processes, the long rolls of fabric are subjected to the heat and steam during passing through a series of concentrated chemical solutions. The fabric holds the greater part of the chemicals but significant amount of chemicals used in preparation step are removed during rinsing. When a fabric is passed through a solution, the amount of water used should be equal to the weight of fabric at each time.
- ***Batch dyeing process***: It is the oldest dyeing process. Batch processes are known as the most common methods used for dyeing textile materials. In the process of batch dyeing, the dye is gradually transferred from a relatively large volume dye bath to the material to be dyed within a relatively long period and

therefore this process is also called as exhaust dyeing. The term, “to exhaust” means the transfer of the dye from the dye bath to the substrate. Textile substrates can be dyed in batch processes in most of the stage of their assembly into a textile product including fiber, yarn, fabric or garment. In addition in this process generally there is a wide flexibility for color selection, beside relatively lower dyeing cost (Perkins 1991). There are three general batch dyeing machines in which only fabric, only dye bath, and both of them were circulated.

Many techniques in the dyeing process possess intricate, special and decorative properties. The dyeing is achieved by the direct application of dye solution onto textiles; whereas, the printing dyeing can be carried out using different specialized techniques (Needles 1986). Dyeing techniques have changed dramatically in 1856 when Sir William Perkin, an English chemist, discovered a new dye. The vibrant mauve color created triggered the emergence of many other scientific discoveries with its tremendous impact on the fashions of the day. The dye which is incidentally discovered has then been applied to dye a piece of silk cloth. As a result it has provided to an unfading coloring. This new dye shortly replaced the natural dye of madder (Garfield 2001; Goetz 2008).

Now, some other common dyeing techniques, and also special printing dyeing techniques will be discussed somewhat in detail:

- ***Resist Dyeing***
  Resist dyeing is an old and decorative aimed technique that dates back to the B.C. and is carried out with the dye penetration hindered in certain parts of the textile product while the rest of the fabric receives the dyes. Common resist dyeing techniques include tie-dyeing, hot wax resist technique, starch paste resist, tritik, and clamping methods (Goetz 2008). The resist fabric dyeing technique is a manual procedure that was directly applied by workers, and used various synthetic dyes and chemical (Akintayo 2013).
  The resist dyeing has been defined as the technique creating patterns on cloth by impeding penetrating of dye or pigment to fabric by Wada (2002). In other words, the resist dyeing is also described as a process in which a certain part of cloth was dyed and deliberately prevented dyeing of other parts (Brito 2002; Choi and Powell 2008). Resist dyeing is a multiple step process in which an impermeable substance such as wax, clay, or resin is applied to portions of a fabric in order to prevent dye from penetrating those areas. After dyeing, the resist material is removed to form pattern leaving undyed space. Repeating this process could allow the creation of poly chrome designs. Resist dyeing requires special materials, knowledge, and skill (Kuttruff 1993; Baldia 2005; Coon 2009).
- ***Tie-dyeing***
  Tie-dyeing as a different form of the resist dyeing is the tying or stitching technique of fabric to prevent the absorption of dye to a particular area (Solomon and Ezra 2015). This process consists of protecting parts of the cloth by tying them up, so that those parts are reserved and the dye cannot fully penetrate

under the ties. The technique seems to have originated in Asia and spread down to sub Indian continent to the Malayan archipelago and also across to Africa. Tie and dye technique was most developed in Indian sub-continent, particularly in Republic of India. This technique of decorating the fabric was very popular all over India, particularly in Rajasthan, Central India, Gujarat and Bombay district (Amubode 2009). Tie-dyed products are perfect mix with local wisdom of unique patterns and colors in cotton fiber, which is a natural material. A simple design process begins with designing the patterns and colors from natural ingredients. These represent the unique nature of the tie-dyeing, which is transmitted from generation to generation (Mayusoh 2015).

In this resist-dyeing process, waxed thread is tightly tied around the areas chosen to resist the colored dyestuff and the fabric is immersed into the dye. The waxed thread is then removed and the fabric is dried. This process can be repeated for each color adding (Alheri 2014). Tie-dyeing techniques can be listed as Circles, Stripes, Tying, Marbling, Pegging, Sewing, Ruching and Spiral. Moreover, there are many special sub-processes of tie-dyeing including Shibori, Leheriya, Bandhini, and Ikat.

- ***Shibori***
  Shibori is actually an old name of the tie-dyeing technique as a Japanese art which consists of binding, tying, twisting, stitching, or wrapping of fabric during the process of dyeing (Lazzarine 2013). In addition this technique includes the particular groups of the resist dyeing (tying resist, folding and tying, folding and pressing between different types of plates resist technique and sewing resist). The Subori word's origin refers the cloth manipulation process which may be applied by the modern dyeing methods (Bitay 2011; Nguyen 2011).
- ***Leheria***
  Leheriya (or Lehariya) is a widely known variation of design in fabrics that is produced by using the technique of tie-dyeing. This technique is distinguished by the natural, ripple effect in mesmerizing colors by using the resist-dyeing technique. Usually two color patterns are used in leheriya. These colors alternate each other in the form of waves. Originally, only two colors red and yellow were used for the leheriya pattern. The dyeing process is accomplished by the tie-resist technique and it creates the patterns formed innumerable waves.
- ***Tsutsugaki***
  Tsutsugaki is the technique of applying of a design being accomplished by pushing of a rice paste resist through a tube (tsutsu). The areas that will not be dyed have to be covered to keep pigment out. Traditionally, this technique that can often be employed to create large, bold patterns was mainly used with indigo dye. Generally, a tsutsugaki textile may, also include the some handed made grey or red colored details on the cloth, after the resist dyeing is completed (Ohsawa et al. 2007; Seton 2010).
- ***Katazome***
  Katazome, which is used in the Japanese-resist dyeing technique and actually a resist paste, is made from rice bran (komon nuka) and powdered sweet rice

(mochiko) (Bin Haji Lias 2007). Resembling the expensive woven brocades, katazome was used to dye inexpensive cotton or linen garments. Therefore, it gained wide popularity and was produced in large quantities to meet the growing demand among the commoners in early modern Japan. In this technique which produces well-defined patterns resembling sharp edged prints rather than the dyed designs the desired divisions of fabric is covered partially with a resist agent that could hinder penetrating of the dye (Toba 2014). This technique expresses the essence of Japanese aesthetics through the use of handmade paper, rice paste, sensitive natural colors, and the thematic materials (Kawano 1987; Boettcher 1987).

Katazome technique uses a paste like wax which is applied using stencils, and the katazome textiles are also mostly dyed by dipping for adding of color (Gunter 2003). Wax may also be used in place of rice paste. Both blue and indigo tones are the colors used very commonly in this process (Hayden 2007).

- ***Batik***

  Batik is the dyeing process, in which the melted wax is applied on the cloth with a special pen called “canting”. The wax used is removed by boiling after the dyeing and fixation steps. Repetitions of these steps may produce the multi-colored patterns (Haake 1989). The natural and unique crack design created with the help of wax can be considered as the most important superiority for the products of the batik-dyeing (Nurhaida et al. 2015; Bhowmik 2011; Ismail et al. 2012; Meutia and Ismail 2012; Borshalina 2015).
- ***Kalamkari***

  Kalamkari is known as one from the oldest practices related with the dyeing and printing made by using the natural dyes onto textiles with the fabulous styles of the surface design involving the use of vegetable dyes (Deshmukh and Ganeshani 2013). This technique is a type of hand painted or block printed method of painting on natural dyes onto cotton or silk fabric with a bamboo pen (Kalam) (Mishra and Patni 2011). The process of “Kalamkari” is fairly elaborate and involves washing, rinsing, soaking and bleaching of muslin cloth. It utilizes mordant and dyes made from natural substances. As a result, several colors like blue, red, yellow and black are obtained. These colors are originally come from indigo, madder, mago bark and iron oxide. The process of dyeing the fabric can take several days to complete. The pieces can be hand drawn or block printed depending on the size and scale of the artwork (Sud and Mathew 2011). There are two main styles of Kalamkari (Purohit 2013).
- ***Ikat***

  Ikat or “Jaspe” is essentially, the type of weaving, in which the warp and weft or both were made tie-dyeing before weaving to create designs on the finished fabric. The term, “ikat” refers to a resist dye technique and is originated from the word “mengikat” meaning ‘to tie’. The ikat technique involves tightly tying a pattern or motif into sections of the warp or weft threads (VanStan 1957). These tied or ikat sections of thread resist the dye when the threads are later submerged in dye (Barrkman 2006). The Ikat technique is a combination of the techniques such as Shibori, Batik and the weaving (Tarui 1990).

- ***Rōketsuzome***

  Rōketsuzome is a traditional wax-resist textile dyeing technique in Japan. This technique has several similarities with batik. They both use the wax as the medium of dye-resist, but they show differences in the sense of tools and textural effects. This technique that is also called as Rozome or Rokechi was known as a way of stamping wax on fabric up to the 7th and 8th century. Then, its popularity somewhat decreased but the interest in this art only increased again in the early 17th century as a stencil-and-dye art. In the 20th century, the passion for Rozome revived again with easy access to local and imported wax. Instead of using the tjanting/canting, this technique utilizes a variety of brushes to produce the finished design. Some of the brushes include Rofude (used to paint the hot wax onto the cloth), Surikomi (for blending color), Irosashi (for fine details), Jizome or Hikizome brush (a big flat brush for background work).
- ***Mordant Dyeing***

  Dyeing of fabrics with natural dyes often leads some problems such as narrow shade range, and lower color fastness of the dyed textiles. Attempts to overcome these problems have been mainly focused on the use of mordant. The term “mordant” is often used for the chemicals including metal with at least two or more valence that increase affinity between the dye and the fiber, and are also used to change the hue of dyes. The different mordant used with the same dye may alter drastically the final color of the dyed fiber, as more dark, or brighter (Shahid et al. 2013). Main function of the mordants used in textiles is to provide the fixation of color in the dyeing or the printing processes especially for fabrics of plant origin such as cotton. In addition, mordant is used to control the reaction between the dye and the fiber in order to obtain different colors. It is added to the dye source and does not serve as a color source its own. In the mordanting process, firstly, fabric is impregnated with the mordant and then the dye reacts with the mordant for forming a chemical bond and attaching it firmly to the fabric during the dyeing process (Abuamer et al. 2014). Therefore, the choice depends on the type of fabric mordant. The aluminum ion is one of the most important mordant known since ancient times. Also, it is known that the iron and copper ions formed a chemical bond with the acidic amino acid side groups (glutamic and aspartic acids) of the peptide chains forming wool backbone and with the chromophore molecules (Manhita et al. 2011).

  On the other hand, mordant dyes forming one class of azo-dyes are characterized by the presence of a hydroxyl group ortho to the azo-group. They are also known as the colored aromatic compounds requiring the presence of a mordant metal such as chromium which could be used to set properly their color on fabrics by forming an insoluble compound. Synthetic mordant dyes (chrome dyes) corresponding to about 30 % of dyes used for wool are especially suitable for black and navy shades. However, the improper use of dichromate leads to the release of the toxic chromium (VI) salt into the environment, and therefore mordant dyes are accepted as very hazardous in terms of the human health (Elmorsi et al. 2010).

The mordanting may generally provide the improved dye performance as well as a wide spectrum of colors on many natural and synthetic fibers with expanded shade ranges and better fastness properties (Kadolph and Casselman 2004). The mordant metal ions act like the electron acceptors capable of forming co-ordination bonds with the dye molecules and making them water-insoluble (Mongkholrattanasit et al. 2011; Kulkarni et al. 2011). The mordants that are used most commonly in natural dyeing can be listed as aluminum potassium sulphate, potassium dichromate, stannous chloride, ferrous sulphate and copper sulphate (Samanta and Agarwal 2009). Improvements in traditional mordanting processes, and selecting of new mordants to replace traditional heavy metal ions has been an important part of the development in the natural dyeing of textiles (Shahid et al. 2013).

- ***Reactive dyeing***

  Nowadays, reactive dyeing especially is one of the most important techniques used for the coloration of cellulosic fibers. The reactive dyes cover a wide range of dyes having varying shades, fastness, and costs as well as high brilliancy, easy applicability and reproducibility (Rashid et al. 2013). With growing popularity of reactive dyes for dyeing of cotton, environmental problems associated with their use have received an intensive attention (Periyasamy et al. 2011). Reactive dyes can also be applied on the materials such as wool and nylon but it needs weakly acidic conditions for the dyeing in the case of nylon. Reactive dyes have a low utilization level compared to the other dyestuff types, because of their functional groups that could hydrolyzed. All reactive dyeing processes consist of three principle steps such as exhaustion, fixation or reaction and washing-off (Waring 1990; Shore 1995).

  In the exhaustion process, the required amount of dissolved dye is added to the dye bath at ambient temperature and then the temperature is gradually raised to the recommended dyeing and fixation temperature, and finally the required amount of salt is added in portions. In the fixation step the fixation or reaction starts by adding to the materials of the required amount alkaline substance. The hydroxide ions may easily diffuse into the cellulose and so the ionization of cellulose is quickly occurred (Aspland 1992). In the washing- off process, all of the hydrolyzed and unfixed dye must be removed to avoid compromising wet fastness. The difficulty of this process is determined by the substantivity of the unfixed dye. The more substantive unfixed dye is, the more difficult the wash-off process (Chen 2006).

- ***Ring Dyeing***

  Essentially, this dyeing technique is based on the dyeing fault occurred by the partial diffusion into fiber of the dyes. The dyes are stained to form a layer of dye onto the fiber surface and thus the appearance resembling a ring of dye can be viewed as cross-sectional around the fiber. This ring-like dye layer prevents further dye diffusion and it leads to poor washing and rubbing fastness of dyed fabric as bad as other staining related fastness properties. Especially, indigo ring dyeing is a unique process that makes denim special and the operations on denim different from all other dyeing types of cotton fabrics. The other techniques of cotton textile dyeing generally requires the multiple application of dyeing to achieve a dark color, with the extreme dye bath, slow production as well as extreme color variation and color fastness. Therefore, the indigo ring dyeing of cotton need to be handled accurately with its various aspects (Choudhury 2006; Akçakoca Kumbasar et al. 2006; Holbert 2011; Uddin 2014).

4.4 Paints and Painting

Paints that are often used for protecting of color are applied also, to provide texture to objects (Ndugu 2013). Painting means to the application of paint, pigment or color to a surface. Painting may be applied to such surfaces as walls, paper, canvas, wood, glass, lacquer, clay, leaf, copper and concrete and it may incorporate multiple other materials including sand, clay, paper, plaster, gold leaf, as well as objects.

There are two common types of paint used today. The first are water-based paints such as latex and acrylic paint, and the second are oil-based paints. The term, “latex” means to the aqueous colloidal dispersion prepared by emulsion polymerization (Yamak 2013). The curing process of such paints is called “coalescence”. The choice of paint is depended on the substrate to be painted and the desired end product. All paints contain the three basic structural components, including of pigment, binder and solvent (Mcintee 2002).

- **Pigment**: This provides the opacity and color of the paint as the part of the paint, which is seen by the eye. White pigments were used widely as a white base, including of white lead (basic lead carbonate, $2PbCO_3{\cdot}Pb(OH)_2$) lithopone (mixed $ZnS/BaSO_4$), zinc oxide (ZnO), antimony oxide (Sb_2O_3) and titanium dioxide (TiO_2) (Ali 2005). Dyes are added to the pigment to attain the desired color. Similarly, fillers that are granular solid ingredient are also used to impart toughness and texture and give the paint certain specialties or to reduce the cost of the paint. Alternatively, some paints contain dyes instead of or in combination with pigments.

  Granular solid ingredient pigments can be classified as natural and synthetic. Natural pigments include various clays, calcium carbonate, mica, silica, and talc. Synthetics would include engineered molecules, calcined clays, blanc fixe, precipitated calcium carbonate, and synthetic fumed silica (Ezeagba et al. 2014). In addition, hiding pigments include titanium dioxide (TiO_2), phthalocyanine blue, red iron oxide and others, which make paint opaque and protect the substrate from effects of ultraviolet light (Kameti 2013). Some pigments such as the lead are toxic. Therefore, white pigments including titanium dioxide are a primary alternative for the pigments that are used for lead paint, previously.

The titanium dioxide used in most paints today is often coated with silica/alumina/zirconium for various reasons such as better exterior durability, or better hiding performance (opacity) promoted by more optimal spacing within the paint film.

Fillers are special type of pigment that serves to thicken the film, support its structure and increase the volume of the paint. Fillers are usually cheap and inert materials, such as diatomaceous earth, talc, lime, barites, clay, etc. Floor paints that must resist abrasion may contain fine quartz sand as filler (Tsegaye 2011). Even though all of the paints may not contain fillers, some paints contain large proportions of pigment/filler and binder.

- **Binder**: It is the film forming component of paint and is therefore the most important ingredient. In water borne paint formulations, latex is often used as a binder and imparts adhesion and has a great impact on properties such as gloss, flexibility and toughness (Farmand 2012). Many binders are too thick to be applied, and they may be used by thinning. The type of the thinner to be used varies with the binder type. The thinner is also called as a vehicle, which it can provide the more easy transfer of the binder to the surface using a brush, roller or sprayer (Johnson et al. 2009).

  Binders typically include synthetic or natural resins such as, polymers and copolymers based on acrylics, polyurethanes, polyesters, melamine resins, epoxies, and/or oils or other monomer species (Acton 2013). Binders that were be categorized according to the mechanisms of drying or curing, are classified also as convertible and non-convertible (Lehnert 1997). Although drying may refer to evaporation of the solvent or thinner, it usually refers to oxidative cross-linking of the binders and is indistinguishable from curing. Some paints form by solvent evaporation only, but most rely on cross-linking processes.
- **Solvent**: This is the bulk of the paint which is used to keep the paint workable when it is wet. After paint is applied to a surface, the solvent evaporates, the pigment and binder will coalesce together to form a uniform coating. The solvent is water for water-based paints, and any oil for oil-based paints.

  Apart from the three main ingredients, paints can have a wide variety of miscellaneous additives which are usually added in small amounts. These additives generally are used in order to modify surface tension, improve flow properties and the finished appearance, increase wet edge, improve pigment stability, impart antifreeze properties, and control the foaming and the skinning. Catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, flatteners (de-glossing agents), and biocides can be listed as other additive types (Aherns 2008). However, the use of additives does not lead to a significant altering in the percentages of individual components in a formulation.

On the other hand, a clear paint like a varnish contains primarily the binder and the vehicle plus some driers. If the pigment is added to provide color and opacity into a varnish, the enamel can be created. Enamels therefore contain the three primary ingredients, such as binder, vehicle and pigment, which found in all paints.

There is actually no chemical bonding between paint and an underlying surface. Paint adheres simply through weak physical interactions. When paint is first applied to a surface, it goes on as a thick wet coating. As the solvent is allowed to evaporate out, the pigment plates which are attracted to one another stack up to form layers. The binder essentially polymerizes to lock together the pigment plates and eventually, a uniform coating formed of binder and pigment is obtained.

Oil paint is a type of slow-drying paint that consists of particles of pigment suspended in a drying oil, commonly linseed oil (Izzo 2010). The viscosity of the paint may be modified by the addition of a solvent such as turpentine or white spirit. Varnish may be added to increase the glossiness of the dried oil paint film. Oil painting is the process of painting with pigments with a medium of drying oil as the binder. Commonly used drying oils include linseed oil, poppy seed oil, walnut oil and safflower oil.

Acrylic paint is a fast-drying paint containing pigment suspension in acrylic polymer emulsion. Acrylic paints are water-soluble but they become water-resistant when they dry. Depending on how much the paint is diluted with water or modified with acrylic gels, media, or pastes, the finished acrylic painting can resemble a watercolor or an oil painting but it has its own unique characteristics. Acrylic paints differ from oil paints, because they have shorter drying times and are soluble in water.

Watercolor is a painting method in which the paints are made of pigments suspended in a water-based solution. Watercolor paint consists of four principal ingredients such as pigments (natural or synthetic, mineral or organic), binder (gum Arabic), additives (glycerin, ox gall, honey), and solvent (water).

Anti-graffiti coatings can impede paint adhesion to the surface and they are invisible to the naked eye. There are two different categories of anti-graffiti coatings. The first, sacrificial coatings are applied to a surface and then removed when graffiti is applied. The surface underneath will be left clean and a new sacrificial coating can be applied. The other types of coating are the permanent coatings that could prevent the adhesion of graffiti to a surface in the first place. Newer coatings are made of charged polymeric materials that form a gel on the surface of the building or substrate. The sufficient adherence without damage to substrates; hydrophobicity; environmentally friendly composition and processing; high UV aging and weathering resistance, and good cleaning efficiency are some of the most important characteristics of anti-graffiti coatings.

The paints that cure by oxidative crosslinking are generally single package coatings. When applied, the process, in which the polymerization of binder component and the formation of crosslinkings occur, starts to progress with oxygen in the air. Classic alkyd enamels would fall into this category. Oxidative cure coatings are catalyzed by metal complex driers such as cobalt naphthenate.

Paints that cure by polymerization are generally one or two package coatings that polymerize by way of a chemical reaction, and cure into a cross linked film. Depending on the composition, it may be needed a pre-drying via the evaporation of solvent. Epoxies and polyurethanes would fall into this category.

There are also paints called as plastisols/organosols made by blending polyvinyl chloride granules with a plasticizer. Other films are formed by cooling of the binder. For example, encaustic or wax paints are liquid when warm, and harden upon cooling. In many cases, they re-soften or liquefy if re-heated.

Recent environmental requirements restrict the use of volatile organic compounds (VOCs), and alternative means of curing have been developed, generally for industrial purposes. In UV curing paints, the solvent is evaporated first, and hardening is then initiated by ultraviolet light. In powder coatings there is little or no solvent, and flow and cure are produced by heating of the substrate after electrostatic application of the dry powder.

Paint can be applied as a solid, a gaseous suspension (aerosol) or a liquid. Techniques vary depending on the practical or artistic results desired.

As a solid (usually used in industrial and automotive applications), the paint is applied as a very fine powder and then baked at high temperature. This melts the powder and causes it to adhere to the surface. The reasons for doing this involve the chemistry of the paint, the surface itself, and even the chemistry of the substrate (the object being painted). This is called "powder coating" an object. Powder coating is a type of coating that is applied as a free-flowing, dry powder. The main difference between a conventional liquid paint and a powder coating is that the powder coating does not require a solvent to keep the binder and filler parts in a liquid suspension form. The coating is typically applied electrostatically and is then cured under heat to allow it to flow and form a "skin". The powder may be a thermoplastic or a thermoset polymer. It is usually used to create a hard finish that is tougher than conventional paint. Powder coating is mainly used for coating of metals. Newer technologies allow other materials such as MDF (medium-density fiberboard) to be powder coated using different methods.

After liquid paint is applied, there is an interval during which it can be blended with additional painted regions (at the "wet edge") called "open time." The open time of an oil or alkyd-based emulsion paint can be extended by adding white spirit, similar glycols such as propylene glycol ether or open time prolongers. This can also facilitate the mixing of different wet paint layers for aesthetic effect. Latex and acrylic emulsions require the use of drying retardants suitable for water-based coatings.

As a gas or as a gaseous suspension, the paint is suspended in solid or liquid form in a gas that is sprayed on an object. The paint sticks to the object. This is called "spray painting" an object. Paint application by spray is the most popular method in industry. In this, paint is atomized by the force of compressed air or by the action of high pressure compression of the paint itself and the paint is turned into small droplets that travel to the article to be painted. Alternative methods are airless spray, hot spray, hot airless spray, and any of these with an electrostatic spray included. There are numerous electrostatic methods available.

Dipping used to be the norm for objects such as filing cabinets, but this has been replaced by high speed air turbine driven bells with electrostatic spray. Car bodies are primed using cathodic primer which is applied by charging the body depositing a layer of primer. The unchanged residue is rinsed off and the primer is stored.

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Chapter 5
Colorants in Health and Environmental Aspects

Abstract The environmental characteristics of colorants (dyes and pigments) cover the topics pertaining to the impact of such compounds on human health and the environment. Effluent aqueous waste containing dye compounds causes serious problems. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry today. Consequently, they have become common industrial environmental pollutants during their synthesis and later during fiber dyeing. This is main requirement for the innovations in the related processes as well as the investigation of appropriate and environmentally friendly treatment technologies. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. Dyes have various effects on human health depending on the application area. Skin irritation and contact dermatitis have been reported for some synthetic dyes and the use of azo dyes made from carcinogenic amines has been banned by legislation in many countries. The researches on alternative and innovative wastewater treatment techniques have focused especially on the use of biological materials. Adsorbents such as activated carbon, zeolite and diatomite have been used as efficiently for cleaning by adsorption of colored wastewaters. In this chapter, a wide range of dyes and pigments are discussed in the context of green chemistry with environmental and health aspects by considering their negative results related with their use.

Keywords Colorants and the environment · Dye · Pigment and health · Toxic dyes · Harmful dyes · Green chemistry

A. Gürses et al., *Dyes and Pigments*, SpringerBriefs in Green Chemistry
for Sustainability, DOI 10.1007/978-3-319-33892-7_5

5.1 Introduction

Today there is a wide spectrum of colors that can be obtained from many plants, insects and fungi. They have been used across the centuries to produce the dyed textiles, artifacts and patterns, as well as to color the skin and hair and even the foods. The discovery and use of such natural colorants has contributed to the formation of a strong and esthetic bond between humankind with nature (Wells 2013). Natural dyes and colorants which are still an essential part of the ecological and cultural heritage of the world, are considered also as a primary source for permanent colors that once were used commonly in the whole world (Cardon 2010).

The terms ‘dye’, ‘pigment’ and colorant are often used incorrectly as though they were synonymous. Although the distinction is primarily a matter of the field of application, the necessary physicochemical characteristics imply that dyes and pigments must be having quite different toxicological and eco-toxicological profiles (Clarke and Steinle 1995). Colorant is the collective term applicable to a dye or a pigment (Von Elbe and Schwartz 1996).

Colorants having heterocyclic rings containing oxygen, nitrogen or sulfur have been used widely, owing to their versatility in the various areas of high technology including textiles, paper, leather, plastic, biological staining, lasers, liquid crystalline displays and ink-jet printers. Additionally, they have been used for specialized applications such as food, drug, cosmetic and photochemical production (Kurtoglu et al. 2010). The color of a product is considered also as the indication of its quality and freshness. Colors are obtained from either natural or synthetic substances (dyes) or from plant or animal sources (pigments) (Frimpong et al. 2014).

Dyestuffs that are used in textile industry give color to the water. Hence, the colored textile wastewaters accumulated in water environment can lead to deteriorate of the aesthetic appearance of the water as well as to decrease of the light permeability. The decrease of the light permeability and amount of decomposed oxygen may cause to the extinction of living beings and restrict the reuse of the water. Furthermore, some dyestuffs contain, also the toxic ingredients. On the other hand, total suspended solids (TSS) levels in the wastewaters from the textile dyeing are the lower, compared to many other industries, but biological oxygen demand (BOD) and chemical oxygen demand (COD) are relatively high (Tüfekci et al. 2007).

An alternative applicable for minimizing the problems related to the treatment of textile effluents is the development of more effective dyeing techniques which could provide the fixation of dye with a higher efficiency onto the fiber. These techniques may also provide the decrease of dye losses in tailings waters with use of less amount dye for the dyeing (Chequer et al. 2013).

5.2 Colorants in Health Aspect

The environmental characteristics of colorants (dyes and pigments) cover the topics pertaining to the impact of such compounds on human health and the environment (Freeman 2014). The rapidly growing food industry requires the new economic and functional ingredients (Campbell 2010). Color is an essential part of the identity of foods and can affect the products' success in the market. The food industry is no longer seeking natural alternatives for synthetic dyes (Ahmadiani 2012).

Eyes are the sensory organs that will be gratify first as visual for foods. This is an old axiom with very significant meaning and depicts how colors in life have importance. People's perception is usually influenced by the appearance of the food and this indicates the flavor. So it is important to note that the color of a food or beverage often dominates over other sources of information regarding the flavor. From various studies it has been observed that color of a food or beverage can play a profound role in flavor perception (Lakshmi 2014).

The use of food additives in food products including the food colorants is an emerging issue, especially in health aspect. The appearance of the food, especially its color is important factor affecting the attractiveness of consumers to consume. Hence, the food colorants become so important in the production of food. Food colorants can be classified as synthetic and natural. Synthetic colorants have been widely used in the food industry due to its effectiveness (Amelia et al. 2013). However, the application of synthetic colorants for the food or beverages can cause toxic and carcinogenic effects. As a consequence, some food scientists try to use natural colorants in order to hinder the negative effects of synthetic colorants (Chengaiah et al. 2010; Jokopriyambodo et al. 2014). Currently, the interest in using natural colorants has increased because of their non-toxicity and beneficial health effects, mainly as antioxidants (Molina et al. 2014). Natural colorants have many disadvantages when compared to synthetic ones, including higher cost in-use and lower stability. However, people have increasingly avoided synthetic colorants, preferring natural pigments, which are considered to be harmless or even healthy (Azeredo 2009).

The conditions required for the use of colorants by the food industry can be listed as the following (Hassan 2010):

- The conservation of original food appearance after processing and during storage. Because while processing, the quality of food may disappear slowly without being realized.
- The ensuring of color uniformity to prevent the seasonal variations occurring in color tone and to make sure that all the food had the same appearance.
- The preserving of a quality level that will be high and stable in every situation, by intensifying the colors that normally found in food.
- The protection of other components such as flavor and vitamins, for conserving of the flavor and nutrients.
- The obtaining of the best food appearance.
- The conservation of the characteristics associated with food.

In order to fulfill the growing demand for natural colorants, plant pigments such as anthocyanins, betalains, carotenoids and chlorophylls are among potentially the best candidates to be developed as the probable commercial food colorants (Othman et al. 2015). One of the most common natural colorants already used in the food industry is anthocyanin extracts and juices (Sirven 2015). Betalains are water-soluble nitrogen-containing pigments, which are synthesized from the amino acid tyrosine into two structural groups: the red-violet betacyanins and the yellow-orange betaxanthins (Azeredo 2009). Betalains, known for a long time as safe colorants for food or other industrial purposes, are phytochemicals that were recently classified as antioxidants (Tesoriere et al. 2004). Carotenoids are yellow, orange, and red pigments present in many commonly eaten fruits and vegetables (Holden et al. 1999). It is known that carotenoids have some medicinal properties. They are widely used also in food and nutraceutical applications (Jaswir et al. 2011).

These colorants are not only important for their colors but also their health-promoting properties such as potent antioxidants, bactericidal, anti-viral, anti-mutagenic and anti-carcinogenic (Beutner et al. 2001; Delgado-Vargas et al. 2000; Castañeda-Ovando et al. 2009; Boo et al. 2012).

Natural and synthetic dyes, especially those used in food stuffs have become potential suspects for causing cancer (Swaroop et al. 2011).

5.3 Textile Colorants

Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry today. In fact the art of applying color to fabric has been known by mankind since 3500 BC, but the first use of synthetic dyes has been discovered by WH Perkins in 1856. Synthetic dyes have provided a wide range of colorfast, bright hues. However their toxic nature has become a cause of grave concern to environmentalists. Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic (Kant 2012).

Over the past few years a growing awareness of the environmental, health-related and social problems, caused by the conventional production of textiles has emerge. Admittedly nowadays natural colorants are hardly used in the textile sector (Ganglberger 2009).

Textile colorants can be divided into decoration colorants and products for textile dying of which 80 % of the total consumption is composed of the latter. The group of decoration colorants includes products as felt-tip pens, pop-up dyes, and transfer dyes. The group of products for textile dyeing includes textile dyes intended for dyeing or covering textiles in larger proportions.

Textile products are decorated typically in two principally different ways, by colorants dissolved or dispersed in water, or by insoluble pigments, which like paints are adhered to the substrate by the assistance of a binding agent (adhesive).

There is no evidence to suggest that the majority of the dyestuffs currently used in textile dyeing and finishing are harmful to human health at the levels of exposure that workers generally face in the factories. However, with long-term or accidental over exposure, there can be potential health hazards and all dyes and chemicals must therefore be treated with care. The most common hazard of reactive dyes is respiratory problems due to the inhalation of dye particles. Sometimes they can affect a person's immune system and in extreme cases this can mean that when the person next inhales the dye their body can react dramatically. This is called respiratory sensitization and symptoms include itching, watery eyes, sneezing and symptoms of asthma such as coughing and wheezing.

Perhaps the most prevalent health problems associated with dyeing and finishing processes arise from exposure to chemicals acting as irritants. These may cause skin irritation, itchy or blocked noses, sneezing and sore eyes. They include formaldehyde-based resins, ammonia, acetic acid, some shrink-resist chemicals, some optical whiteners, soda ash, caustic soda and bleach. Certain reactive, vat and disperse dyes are also recognized as skin sensiters (Ahmed et al. 1998).

A dermal exposure can be expected to take place by skin contact during use of the product and of the colored/dyed textile. The duration of contact exposure of the skin will vary but may cause migration of chemical substances from the textile colorants to the skin, possibly helped by sweat (Hansen 2005).

5.3.1 The Advantages and Disadvantages of Using the Natural Dyes in Textile Industry

Clothes dyed with natural colors could be sold at higher prices. In addition, the applications of natural dyes in the textile industries have the following advantages.

- Health and safety aspects of natural dyes: Though all natural dyes are not 100 % safe they are less toxic than their synthetic counterparts. Many of the natural dyes like turmeric, annatto and saffron are permitted as food additives. Many natural dyes have pharmacological effects and possible health benefits.
- They are obtained from renewable sources.
- Natural dyes cause no disposal problems, as they are biodegradable.
- Practically no or mild reactions are involved in their preparation.
- They are unsophisticated and harmonized with nature.
- Many natural dyes have the advantage that even though they have poor wash fastness ratings, they do not stain the adjacent fabrics in the washing process because of the non-substantive nature of the dye towards the fabric. An exception to this is turmeric, which shows substantivity for cotton.

- Natural dyes are cost effective
- It is possible to obtain a full range of colors using various mordants.

Disadvantages of the use of natural dyes in textile industry can also be listed as the following (Sahoo 2014):

- The extraction from the raw materials is time consuming.
- Availability of the natural dyes is limited.
- As the natural dyes are extracted from plants mostly, they are dependent on the growing seasons, which is unlike the synthetic dyes that are produced in the laboratories.
- Even though natural dyes produce bright colors and variety of shades but tend to fade faster than the synthetic dyes.
- Consistency is an issue as no two dye lots are identical due to the impurities in them.
- Some mordant used along with natural dyes may to toxic to an extent. Alum is safer to use though entirely not nontoxic.
- Some fibers such as silk and wool can be dyed by simply dipping them in the dye but cotton requires a mordant.
- Synthetic fibers, which are becoming widely popular, cannot be dyed with natural dyes.

5.3.2 Cosmetic Colorants

Cosmetics are the materials applied via rubbing, pouring, sprinkling or spraying, to the human body to purge, beautify, promote attractiveness, or alter the appearance (Fischer 1973).

From a dermatologist point of interest, cosmetics may be grouped as: (a) skin-care cosmetics (cleansing agents, moisturizing agents, etc.), (b) hair-care cosmetics (shampoos, hair colorants, styling agents, etc.), (c) face-care cosmetics (facial foundations, powders, eye shadows, mascara, lipsticks, etc.), (d) nail-care cosmetics (nail varnishes, paint removers, etc.), (e) fragrance products (deodorants, aftershaves, perfumes, etc.), and (f) ultraviolet (UV) light screening preparations (Nigam 2009).

The dyes such as, Quinoline Yellow, Sunset Yellow,Tartrazine and Brilliant Blue FCF are known as four main synthetic colorants which were used widely as additives in cosmetic products (Vallvey et al. 1997).

Although, cosmetic products have rarely been associated with serious health hazards, this does not mean that cosmetics are always safe to use, especially with regard to possible long-term effects as the products may be used extensively over a large part of the human lifespan. Many cosmetics, including primarily the hair dyes and shampoos, may contain ingredients classified as the probable carcinogens for human. Furthermore, many of them may also contain “penetration enhancers” increasing penetration through the skin (Nigam 2009).

Fig. 5.1 The examples of hair dyed in various colors

Hair colorants are usually classified according to how long the color lasts and how durable it is on the hair. There are temporary, semi-permanent and permanent colors—these also imply the degree of coverage of depth of coloring (Brown 1987). Hair coloring involves the use of chemicals capable of removing, replacing and/or covering up pigments naturally found inside the hair shaft. Figure 5.1 shows some examples of hair dyed in various colors. Use of these chemicals can result in a range of adverse effects, including temporary skin irritation and allergy, hair breakage, skin discoloration and unexpected hair color results.

Dyes and color modifiers can be sensitizers; that is, can cause allergic reactions such as rashes and other skin irritations. The dyes and modifiers, which contain the amine group, tend to be sensitizers (Brown 1987). Additionally, there is ongoing debate regarding more serious health consequences of hair dye usage, including lead poisoning. Even, it is argued that some hair dyes may be carcinogenic for human. However, aromatic amine hair colorants do exhibit possible carcinogenic or mutagenic effects in animal studies and these are suggestive of potential human health problems. Mutagens are caused to a relatively permanent change in hereditary material. The utility of many organic colorants employed in cosmetic products is restricted by their instability on exposure to light (Thomas 1966).

Cosmetic tattoos (permanent make up) to mimic eye, lip or eyebrow-liner, have also become increasingly popular (Kilmer and Anderson 1993). Tattoos or permanent make-up are simply performed by injection of colorants into the skin using solid needles. Injury of the skin and the application of unregulated colorants cause health problems in humans. The composition of colorants used for tattooing has changed. In the past, the tattoo colorants predominantly consisted of inorganic compounds (Lehmann and Pierchella 1988) whereas nowadays, in most cases, organic pigments are used. Since tattoo compounds, in comparison with cosmetics, are not yet officially controlled, the origin and chemical structure of these coloring agents are hardly known. Consequently, neither the tattoo artist nor the tattooed patient usually has information about the compounds punctured into the skin (Vasold et al. 2008).

5.4 Colorants with the Environment Aspect

Nowadays, the public has become more sensitive toward the protection of the environment and thus, an increased general awareness about the potential adverse effects of industrial effluents contaminated with various pollutants including dyes onto the environment has emerged (Yadav et al. 2012). Though the rapid industrialization is the best way to achieve economic growth, it affects human health directly or indirectly by escaping wastes into water bodies. Unfortunately, the most of dyes used are left into conventional wastewater treatment processes (Karthik et al. 2014).

The environmental issues associated with residual dye content or residual color in treated textile effluents are always a concern for each textile operator that directly discharges, both sewage treatment works and commercial textile operations, in terms of respecting the color and residual dye requirements placed on treated effluent discharge (Carmen and Daniela 2012).

Environmental legislation obliges industries to eliminate color from their dye containing effluents before disposal into the water. Several different methods are reported in the literature for the removal of pollutants from effluents shown in Table 5.1.

Methods for color removal of dye can be divided into three categories, including biological, chemical and physical (Robinson et al. 2001).

Currently, most treatments used in the removal of textile dyes are based on physical and chemical methods, as the cheaper and more effective alternatives (see Table 5.1). Also, the biological processes are fewer effective for color removal (Gürses et al. 2006).

Environmental problems associated with the textile industry are typically those associated with water pollution caused by the discharge of untreated effluent. Effluent are generally hot, alkaline, and strong smelling, and colored by chemicals used in coloring process. Some of the chemicals including of dyes and pigments may be toxic, or can increase the dissolved oxygen demand of receiving waters and thereby threaten the aquatic life and general water quality. Moreover, their effects on the organisms found in the environment may be either short term (acute) or long term (chronic).

In relation to the textile industry, four potential routes of colorants to enter the environment have to be considered. These can be listed as routine the effluent or emissions, the disposal of surplus materials and process residues, accidentally releasing, and the disposal of used packages (Solid waste) (Shaikh 2009).

The problems in the environment caused by the use of dyes are concisely given below:

- Depending on exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms.
- The presence of very small quantities of dyes in water (less than 1 mg/L) is highly visible due to their brilliance.

Table 5.1 Different processes or reagents that are used for color removal, with their advantages and disadvantages

Process or reagent	Advantages	Disadvantages
Fenton's reagent	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-products
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Clay	Good removal of wide variety of dyes	The smaller particle size of the clays make them difficult to separate from water phase
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production

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- The greatest environmental concern with dyes is their absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously influence on the food chain.
- Dyes can remain in the environment for an extended period of time, because of high thermal and photo stability. For instance, the half-life of hydrolyzed Reactive Blue 19 is about 46 years at pH 7 and 25 °C.
- Many dyes and their breakdown products are carcinogenic, mutagenic and/or toxic to life. Dyes are mostly introduced into the environment through industrial effluents. There is ample evidence of their harmful effects. Triple primary

cancers involving kidney, urinary bladder and liver of dye workers have been reported.
- Textile dyes can cause allergies such as contact dermatitis and respiratory diseases, allergic reaction in eyes, skin irritation, and irritation to mucous membrane and the upper respiratory tract.

Public perception of water quality is greatly influenced by the color. So, the removal of color from wastewater is often more important than the removal of the soluble colorless organic substances. Removal of the dyes from the textile wastewater is often very costly, but a stringent environmental legislation has stimulated the textile sector in developing wastewater treatment plants.

5.4.1 Waste Dye Treatment

Dye wastes represent one of the most problematic groups of pollutants because they can be easily identified by the human eye and are not easily biodegradable (Ong et al. 2011). Dyes in wastewater that can obstruct light penetration and are highly visible, are stable to light irradiation and heat and also toxic to microorganisms (Ejder-Korucu et al. 2015). Dyes in wastewater can be eliminated by various methods. The wastewaters from the dye house are generally multi-colored. The dye effluents disposed into the land and river water reduce the depth of penetration of sunlight into the water environment, which in turn decreases photosynthetic activity and dissolved oxygen (DO). The adverse effects can also spell disaster for aquatic life and the soil (Babu et al. 2007).

Industrial wastewater treatment generally consists of three or four stages, including preliminary, primary, secondary, and tertiary and/or advanced.

- Preliminary treatment includes neutralization and mixing of the waste. The objective of preliminary treatment is the removal of coarse solids and other large materials often found in raw wastewater.
- Primary treatment involves processes such as screening, sedimentation, flotation, and flocculation, all designed to remove dirt and grit, undissolved chemicals, and fibers. The objective of primary treatment is the removal of settle able organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming. Approximately 25–50 % of the incoming biochemical oxygen demand (BOD_5), 50–70 % of the total suspended solids (SS), and 65 % of the oil and grease are removed during primary treatment.
- Secondary treatment consists primarily of aerobic and/or anaerobic biological transformation processes, as well as adsorption to coagulants (i.e. lime). The objective of secondary treatment is the further treatment of the effluent from primary treatment to remove the residual organics and suspended solids.

- The tertiary and/or advanced treatment step (also known as the polishing step) involves capturing or destroying chemical and colored wastes that have survived the first three stages (Park and Shore 1984). Tertiary and/or advanced wastewater treatment is employed when specific wastewater constituents which cannot be removed by secondary treatment must be removed.

The wastewaters discharged by some industries under uncontrolled and unsuitable conditions are caused on many significant environmental problems. The importance of the pollution control and treatment is undoubtedly the key factor in terms of the future of humanity. If a textile mill discharges the wastewater into the local environment without any treatment, it will have the serious negatives imparts on natural water bodies and lands in the surroundings. Moreover, textile industry is one of the major industries in the world which provide employment without required no special skills and have a major role in the economy of many countries.

There are the three different typed fibers including of cellulose fiber, protein fiber, and synthetic fiber, which are used in the manufacture of various textile products. Each type of fiber is dyed with different types of dyes. Cellulose fibers are dyed using reactive dyes, direct dyes, napthol dyes and indigo dyes. Protein fibers are dyed using acid dyes and lanaset dyes. Synthetic fibers are also dyed using disperse dyes, basic dyes and direct dyes (Ghaly et al. 2014).

Textile industry effluents are extremely variable in composition and vary from plant to plant depending upon the processes used in the industry. Main characteristics of a typical textile wastewater are given in Table 5.2 (Verma et al. 2012).

High values of chemical oxygen demand (COD) and biological oxygen demand (BOD_5), presence of particulate matter and sediments, and oil and grease in the effluent causes depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system. Effluent from textile mills also contains chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat (Hussein 2013; Wang et al. 2011; Joseph Egli Italia srl 2007).

Table 5.2 Main characteristics of a typical textile wastewater

Parameters	Range
pH	2–14
Temperature (°C)	35–45
BOD_5 (mg/L)	110–5500
COD (mg/L)	131–17900
TDS (mg/L)	47.9–6106
TSS (mg/L)	64–23900
Color(Pt-Co)	>200
Turbidity (NTU)	15–5700

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5.4.2 Azo Dye Pollution

The polluting effects of dyes against aquatic environment can be also the result of toxic effects due to their long time presence in environment (i.e. half-life time of several years), accumulation in sediments but especially in fishes or other aquatic life forms, decomposition of pollutants in carcinogenic or mutagenic compounds but also low aerobic biodegradability (El-Sayed et al. 2013). Due to their synthetic nature and structure mainly aromatic, the most of dyes are non-biodegradable, having carcinogenic action or causing allergies, dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system (Hijazi et al. 2015). Moreover, various azo dyes, mainly aromatic compounds, show both acute and chronic toxicity. It is known that high potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs, and also formation of hemoglobin adducts and disturbance of blood formation (Karthikeyan and Jothivenkatachalam 2014). The lethal concentration values (LD_{50}) reported for aromatic azo dyes are in the range of 100 and 2000 mg per kg body weight. LD_{50} determination is a simple preliminary assessment about the toxicity of a compound which is based on determination of the median lethal dose which is capable of killing 50 % of animals under stated conditions. In terms of signs or symptoms, LD_{50} is redefined as the dose effective for producing a certain sign in 50 % of the experimental animals (Kelle et al. 2013; Carmen and Daniela 2012).

Azo dyes-contaminated effluents have emerged as a serious issue because of their negative impacts on water ecosystems and human (Jamil et al. 2009; Mahmoud et al. 2011). Several azo dyes can cause the genesis of malignant tumors due to DNA damage (Mahbub et al. 2015). The higher carcinogenic potential for a dye having the electron-donating substituent in ortho and para positions may be expected, but the protonation of amino groups may cause a reduced toxicity. Some of the best known azo dyes and their breakdown derivatives inducing cancer in humans and animals are benzidine and its derivatives, and also a large number of anilines, nitrosamines, and dimethylamines (Börnick and Schmidt 2006).

In environmental systems, azo dye reduction occurs by biological, chemical, or photochemical means. Many bacteria, in both aerobic and anaerobic environments, can perform the reduction of azo dyes (Spadaro 1994). The reduction of azo dyes may emerge also by a chemical redox process which occurred in anaerobic sediments at the bottom of stagnant or brackish waterways (Nam 1998).

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