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Chapter

Structure and Properties of Dyes and Pigments

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Abstract

Colour is one of the elements of nature that makes human life more aesthetic and fascinating in the world. Plants, animals, and minerals have been used as primary sources for colourants, dyes or pigments since ancient times. In our daily life, we know about many substances which have specific colours. These are the substances which are used as colourants i.e.; colour imparting species. Both dyes and pigments are coloured as they absorb only some wavelength of visible light. Their structures have Aryl rings that have delocalized electron systems. These structures are said to be responsible for the absorption of electromagnetic radiation that has varying wavelengths, based upon the energy of the electron clouds. Dyes are coloured organic compounds that are used to impart colour to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. A Dye is a coloured compound due to the presence of chromophore and its fixed property to the acid or basic groups such as OH, SO₃H, NH₂, NR₂, etc. The polar auxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of the fabric structure. Pigments are organic and inorganic compounds which are practically insoluble in medium in which they are incorporated. Dyes and pigments are the most important colourants used to add colour or to change the colour of something. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. This chapter is devoted to the structure and properties of dyes and pigments.

Keywords: Structure, Colourants, Chromophore, Auxochrome

1. Introduction

Colour provides a significant glimpse of our world. Everyday materials we tend to use different kinds of materials like - textiles, paints, plastics, paper, and foodstuffs. Colours make them most appealing. In summer there is a wild burst of colourful flowers and new leaves of various shades of green on trees [1]. However, in contrast, autumn makes the beautiful impression with green leaves turn to brilliant shades of yellow, orange, and red. Colour derives from the spectrum of light interacting in the eye with the spectral sensitivities the light receptors [1, 2].

A dye is nothing but a coloured substance that has an affinity to the substrate to which it is being applied. The dye is applied in an aqueous solution and needs a mordant to boost the fastness of the dye on the textile fibre. The pigment may be a material that modifies the colour of mirrored or transmitted light as the result of wavelength-selective absorption. Pigments are used for colouring paint, ink, plastic, fabric, cosmetics, food and other materials.

Both dyes and pigments appear to be coloured as a result of absorption of some wavelengths of light more than others. However, there are some basic differences between the dyes and pigments

- The major difference between the dyes and the pigments is that particle size of pigments is much higher as compared to dyes. Due to this small particle size dyes are not UV stable whereas pigments are UV stable.
- Dyes after dissolving in liquid are absorbed on the material while pigments make a suspension with a liquid that bonds with the material surface.
- Dyes are generally soluble in water while pigments are almost insoluble in water.
- Most of the dyes are organic while most of the pigments are inorganic
- Dyes are available in large number in the market while the number of pigments is very less.
- Dyes impart colour by selective adsorption while pigments adsorb colour either by selective adsorption or by scattering of light.
- Dyes are combustible while pigments are non-combustible.
- Dyes have a short lifetime in comparison to pigments.

Over the years, man has used colouring matters, which are known as dyes and pigments, for their aesthetic qualities and used them to embellish various articles and the world in which he lived. Indigo, the oldest known dye, was discovered in India; Tyrian purple (or Royal Purple) was discovered in the ancient city of Tyre; Alizarin was discovered among the Turks; and Cochineal was discovered among European and Mexican dyers [3]. Indigenous dye-yielding plants have been discovered in almost every area of the world. The first synthetic dyes were found in the early twentieth century. Parenteral administration was not formulated until the 1930s: methylene blues and methyl violet, for example, were used to treat leprosy and filariasis, respectively [4]. Following World War II, the use of intravenous dyes for medicinal purposes decreased rapidly. Just a few dyes, such as patent blue V or fluorescein, are still used as diagnostic drugs today [5].

The textile industry now uses more synthetic dyes. Coal tar and petroleumbased intermediates are the two main sources of these chemicals. Powders, granules, pastes, and liquid dispersions are all available [6, 7]. Active ingredient concentrations usually vary from 20 to 80 percent. The textile dye segment is distinguished by the introduction of new dyes. These new dyes are produced on a regular basis to meet the demands of new technologies, new types of fabrics, detergents, and developments in dyeing machinery, as well as to address the significant environmental issues posed by some existing dyes [8–10]. With the rapid shift in the textile industry's product profile, from high-cost cotton textiles to durable and flexible synthetic fibres, the pattern of dye use is also shifting rapidly. Polyesters now account for the majority of dye use. Disperse dyes, which are used in Polyesters, are expected to expand at a faster pace as a result. Textile dyestuffs may be grouped into the following groups for better comprehension if general dye chemistry is used as one of the classification criteria as acid dyes, direct dyes, azoic dyes, disperse dyes, sulphur dyes, reactive dyes, basic dyes, oxidation dyes, mordant dyes (chrome dyes) and vat dyes [11–15].

2. Historical background of dyes and pigments

In the ancient age usually used all the dyes were natural. Some of the natural dyes used in ancient age were alizarin and indigo. Indigo is probably the oldest known dye obtained from the leaves of dyers woad herb *Isatis tinctoria*, and the indigo plant *Indigofera tinctoria* [16]. Early dyes were obtained from animal, vege-table or mineral sources, with no to very little processing. The first synthetic dye, mauve, was discovered serendipitously by William Henry Perkin in 1856. The discovery of mauveine started a surge in synthetic dyes and inorganic chemistry in general.

Artists invented the first pigments—a combination of soil, animal fat, burnt charcoal, and chalk—as early as 40,000 years ago, creating a basic palette of five colours: red, yellow, brown, black, and white. In the early age man used earth pigments on cave walls such as yellow earth (ochre), red earth (ochre) and white chalk. Ochres are probably the oldest known pigments, which are coloured clays found as soft deposits within the earth [17–21].

2.1 Reason for the colour of a dye

Many theories have been given to correlate the colour of dyes with their molecular structure. In 1876, Otto Witt, a German Chemist observed that the colour of a dye is due the certain groups containing multiple bonds known as chromophores. Some examples of the chromophores are nitro group(-NO₂), nitroso group(-NO), carbonyl group(-CO-), ethylenic bond(-C=C), acetylenic bond etc. As the number of chromophores increases for a dye, the colour of the dye also deepens [17–21].

He also observed that not only the chromophores are responsible for the deepening of colour but also there are certain groups which itself does not act as the chromophore but the presence of which deepens the colour of the dye. These groups are known as Auxochromes. Some examples of the auxochromes are -OH, -NH₂, -NHR, -NR₂, X (Cl, Br or I), COOH. 1,3-Dinitronapthalene (**Figure 1**) is pale yellow but the dye Martius Yellow (2,4-Dinitro-1-naphthol) is orange-red (**Figure 2**) [17–21]. Here group -OH is acting as the autochrome as the presence of it has deepened the colour of 1,3-Dinitronapthalene.

To explain the origin of colour, Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT) are proposed in modern time. The vital difference between the VBT and MOT is that in VBT electrons are treated in pairs while in MOT electrons are treated singly [17–22].

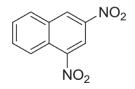


Figure 1. 1, 3-Dinitronaphthalene.

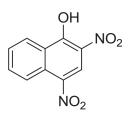


Figure 2. 2,4-Dinitro-1 naphthol.

I.Valence bond theory (VBT): According to VBT, in the ground state the electron pairs of a molecule are in a state of oscillation and absorb a photon of appropriate energy and get excited when placed in the path of a beam of light. The wavelength of a photon of light adsorbed depends upon the energy difference between the ground state and the excited state.

II. **Molecular orbital theory (MOT):** According to MOT, whenever a molecule absorbs a photon of light, one electron is transferred from bonding (nonbonding) orbital to an anti-bonding orbital. Based on different type of electron present in a molecule, different types of electronic transitions are possible.

3. Nomenclature

The chemical names of dyes are very complicated hence trade names are more popular instead of their chemical names. From the ancient time humans have tried to extract the dyes from plants and other natural sources to colour their clothes and other belongings, such dyes are known as Natural Dyes. Indigo and Alizarin are two examples of natural dyes. As the natural dyes have very few colours and shades so now a day's most of the used dyes are synthetic dyes having several colours and shades. Almost all synthetic dyes are aromatic and obtained from coal-tar [22]. Hence synthetic dyes are also called coal-tar dyes. Dyes can be classified by the following ways;

I.**Based on their constitution:** In this classification dyes are classified based on the functional group to which the dyes owe their colour. Some examples are *azo dyes*, *nitro dyes*, *nitroso dyes*, *triphenylmethane dyes*, *indigoid dyes*, *phthalein dyes*, *acridine dyes etc*.

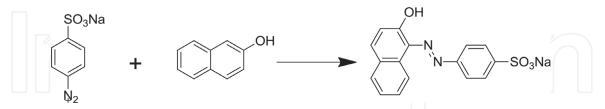
- II.**Based on their application:** The colouring of dye on a particular fibre depends on the nature of both the dye and the fibre. A dye molecule can be attached to fibre by following methods;
 - Covalent Bonds
 - Hydrogen Bonds
 - Ionic Bonds
 - Van Der Waals Forces

Based on application dyes can be categorised as follows;

I.**Acid dyes:** The sodium salt of azo dyes containing sulphonic acid (-SO₃H) and carboxylic acid(-COOH) groups are called acid dyes. To colour the

fabric from these dyes the acidic solution of these dyes is used. These can be used to colour wool, silk, nylon and polyurethane fibres. The affinity of acid dyes for nylon is very high due to the higher protonation of the free amino group present in polycaprolactam fibres. Orange-I (**Figure 3**), orange-II, methyl orange and congo red are some examples of it [22, 23].

The dye orange I and orange II can be obtained by coupling diazotised sulphonic acid with α and β - Naphthol respectively.



Diazotisedsulphonic β-Naphthol Orange-I acid sodium salt

- II. Basic dyes: Those dyes which are salts of coloured bases containing amino or dialkylamino group as autochrome is known as Basic dyes. These include triphenylmethane and azo dyes. Modified nylons and polyesters can be dyed with the help of these dyes [22, 23]. Some examples of basic dyes are aniline yellow (Figure 4), butter yellow (Figure 5) and chrysodine G (Figure 6).
- III.Direct or substantive dyes: These are water-soluble dyes hence they can be applied to the fabric directly [22, 23]. Congo red and Martius yellow (Figure 7) are two examples of these dyes.
- IV.**Disperse dyes:** These are water-insoluble dyes and applied to the fabric in the form of a dispersion in presence of some stabilising agent such as phenol, cresol or benzoic acid. The two examples of disperse dyes are Celliton fast pink B and Celliton fast blue B [22, 23].

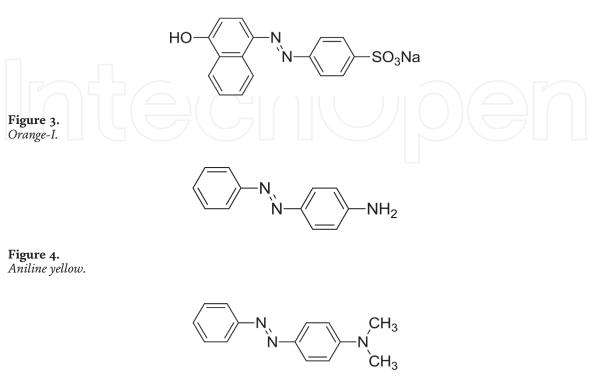


Figure 5. *Butter yellow.*

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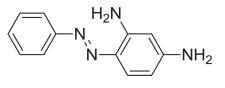
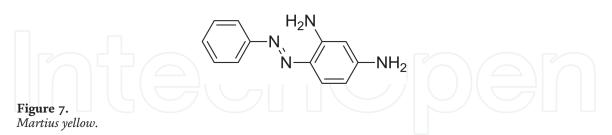


Figure 6. *Chrysodine G.*



- V.**Fibre reactive dyes:** These dyes contain a reactive group which combines directly with the hydroxyl or amino group of the fibre. As a permanent bond formed between the fibre and dye in this case so the colour of the dyed fabric is very fast and has a long life [22, 23].
- VI. **Ingrain dyes or insoluble azo dyes:** These constitute about 60% of total dyes used. These dyes are obtained by the coupling of phenols, naphthols, arylamines, aminophenols. These dyes are adsorbed only on the surface of the fabric, colouring by this dye is not so fast. These can be used to dye cellulose, silk, nylon and leather [22, 23]. Para red (**Figure 8**) is an example of such a class of dye. Para red (**Figure 8**) dye can be prepared as follow:

These dyes are also used in foodstuffs, cosmetics, drugs and as an indicator in chemical analysis.

VII. Vat dyes: Vat dyes are insoluble in water so they cannot be used directly for dyeing. They are first reduced to soluble colourless form (leuco form) with a reducing agent such as an alkaline solution of sodium hydrosulphite. Under these conditions, the leucoform develops an affinity for cellulose fibres [22, 23]. Hence these dyes are mainly used to dye cotton fibre. The example of vat dyes is indigo (Figure 9).

VIII.**Mordant dyes:** Those dyes which do not bind directly but require a mordant to dye the fabric directly come under this category. The mordant act as the binding agent between the fibre and the dye.

Metal ions are used as mordants for the acid dyes while tannic acid is used as the mordant for basic dyes. The desired fabric is first soaked in the suitable metal salt and then this soaked fibre is dipped in the solution of dye when insoluble coloured complexes formed on the fabric. These insoluble coloured complexes are called

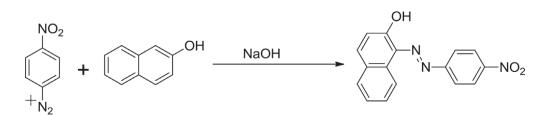


Figure 8. Para red.

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Figure 9. Indigo or Indigotin (Leuco form).

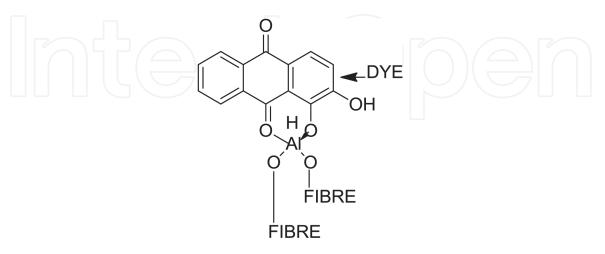


Figure 10. Alizarin-aluminium fibre complex (rose red lake).

lakes [22, 23]. So, the metal ions first get attached to the fabric and then the dye molecules are linked to the metal ion through covalent and or coordinate bond (**Figure 10**).

4. Classification of dyes based on their constitution

4.1 Azo dyes

These dyes constitute the largest part of the synthetic dyes. The chromophore of the azo dyes is aromatic system joined to the azo group and auxochromes are NH₂, NR₂, OH.

Azo dyes are classified as the number of azo group in the molecule such as monoazo, diazo and triazole etc. The characteristic of two important azo dyes methyl orange (**Figure 11**) and congo red can be described as follows:

4.1.1 Methyl orange

It is obtained by coupling of N, N-dimethylaniline with diazotised sulphanilic acid. **Properties:** Methyl orange is a colouring dye for the wool and silk but its colour fades on the exposure to the light and washing. Usually, it is not used as a dye but

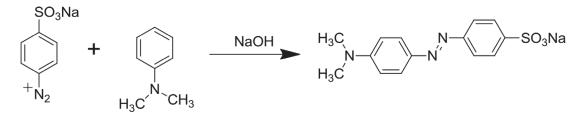


Figure 11. *Methyl Orange.*

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used as an indicator in the acid–base titrations. The pH range of methyl orange is 3.1–4.4. It is yellow in basic solutions (above pH 4.4) while red in acidic solutions (below pH 3.1) [24–26]. The colour change takes place because of the change in the structure of ions in acidic and basic medium. In acidic medium, the ion contains p-quinonoid chromophore while in basic medium ion contains azo chromophore (**Figure 12**).

4.1.2 Congo red

Congo red (**Figure 13**) is the example of diazo dye as it contains two azo groups. It is obtained by the coupling of tetrazotised benzidine with two molecules of napthionic acid (4-aminonapthalene-1-sulphonic acid).

Properties: it is a direct dye and sodium salt of this dye gives red colour on the applied cotton. As on addition of acid, its colour changes so it is also not used as a dye generally. Mostly it is used as an indicator. It is blue in acidic solution (below pH 3) and red in solutions (above pH 3). The change in colour from red to blue in the acidic solution is due to the resonance among charged canonical structures.

4.2 Triphenylmethane dyes

These are the derivatives of -NH₂, -NR₂, and -OH groups in the rings. The compound obtained by this method are generally colourless and called leuco bases. On oxidation, these are converted to the corresponding colourless tertiary alcohols called carbinol bases. These carbinol bases readily change from the colourless benzenoid form to the coloured quinonoid forms in the presence of acids due to salt formation, which is known to be dye [26–30]. The structure and properties of two important triphenylmethane dyes can be discussed as follows;

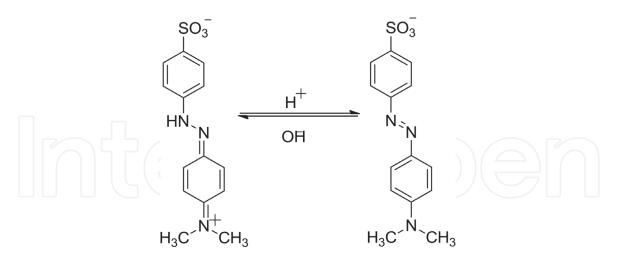


Figure 12. *Red (acidic medium) yellow (basic medium).*

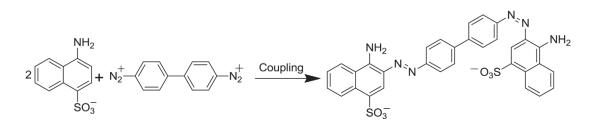


Figure 13. Congo red.

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4.2.1 Malachite green

It is used for dying wool and silk directly and cotton mordanted with tannin. The colour of it fades slowly on the addition of acid and base (**Figure 14**).

4.2.2 Crystal violet

A weakly acidic solution of it is purple, a strongly acidic solution is green and still more acidic solution is yellow (**Figure 15**).

4.3 Phthalein dyes

4.3.1 Phenolphthalein

It is insoluble in water but dissolves in alkalies to form a deep red solution. When an excess of strong alkali is added, the solution of phenolphthalein becomes colourless again. Because of the colour change, it is used as an indicator in acid–base titrations. It is also a powerful laxative (**Figure 16**).

4.3.2 Fluorescein

It is a xanthan derivative. In properties, it more closely resembles phthalein dyes. It is a red powder insoluble in water. It dissolves in alkalies to give a reddishbrown solution which, on dilution, gives a strong yellowish-green fluorescence (**Figure 17**).

4.3.3 Alizarin

It is one of the most important anthraquinone dye. It occurs in madder root in form of its glucoside called, ruberthyric acid.

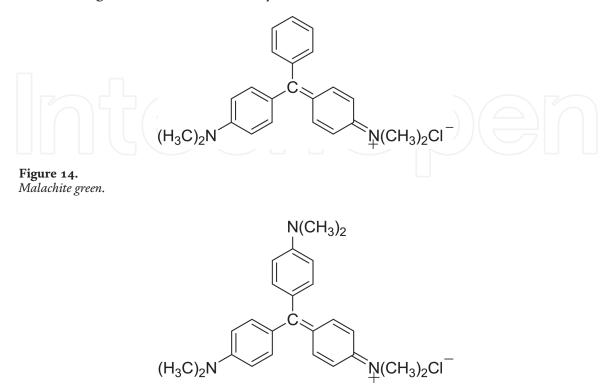
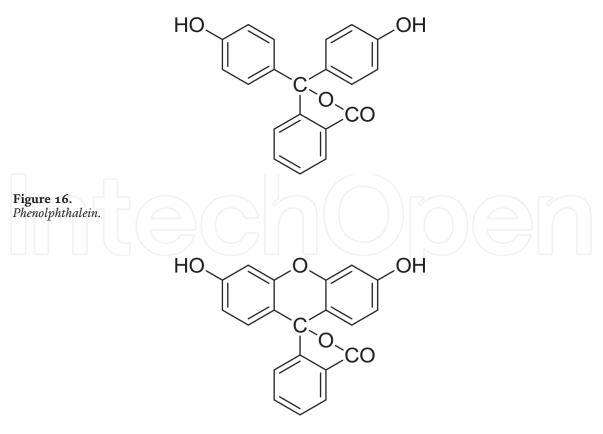


Figure 15. *Crystal violet.*





On reduction with zinc dust, it gives anthracene. This implies that alizarin is a derivative of anthracene. It forms ruby red crystals, insoluble in water and alcohol but dissolves in alkalies to form purple solution, sublimes on heating.

It is a mordant dye, and the colour of the lake depends on the metal used. Aluminium gives a red lake, ferric salts give violet-black while chromium salts form a brown-violet lake. It is also used as a purgative (**Figure 18**).

4.3.4 Indigo

It is the oldest vat dye known. India is the birthplace of Indigo (**Figure 19**). A fusion of indigo at a low temperature produces anthranilic acid.

It is a dark blue powder, with coppered lustre, m.p. 663 K. It is insoluble in water and most organic solvents. It is widely used for dyeing cotton. The quality of colour is excellent and is stable to light, washing etc. It is also used in printing inks [26–30].

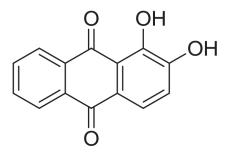


Figure 18. Alizarin.

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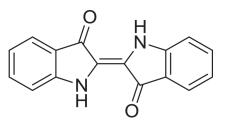


Figure 19. Indigo.

5. Pigments

Those organic and inorganic substances which are widely used as surface coatings, employed in ink, plastic, rubber etc. to impart colour. A large number of pigments are used for commercial manufacture of paints.

5.1 History of pigments

Pigments are believed to be 3.5 lakh to 4 lakh years old. They have been reported in a cave at Twin Rivers, near Lusaka, Zambia. Blue pigment was derived from lapis lazuli. Pigments based on minerals and clays often bear the name of the city or region where they were originally mined. Synthetic pigments are believed to be introduced in early second millennium BCE. White lead 2PbCO₃. Pb(OH)₂ and blue frit (Egyptian Blue) also known as calcium copper sulphate CaCuSi₄O₁₀ are the two examples of early synthetic pigments [17–30].

5.2 Classification of pigments

Pigments are mainly classified into two types:

- 1. White pigments
- 2. Coloured pigments

However, they may differentiate broadly into two category organic & inorganic pigments (**Table 1**) [23–26].

S.No.	Organic pigments	Inorganic pigments
1.	Pthalocyanines, Quinacidrones, Dioxazenes, Napthols, and other pigments made in the lab are examples	Examples include phthalocyanines, quinacridones, dioxazenes, napthols, and other lab-made pigments
2.	Plants and plant products are the primary source of organic pigments	Topical cosmetics, as well as dirt, are used to make inorganic pigments
3.	Carbon chains or carbon rings are still found in Organic Pigment molecules.	Metal cations are present in an array shape with nonmetallic anions in the molecules of Inorganic Pigments. This arrangement prevents the pigments from dissolving in the solvent or the plastic.
4.	Organic pigments have a high index of refraction	Inorganic pigments have significantly lower values
5.	Organic pigments are transparent	Most inorganic pigments are opaque

Table 1.

Difference between Organic & Inorganic Pigments.

5.2.1 White pigments

They are of various types. The composition, properties and applications of some white pigments can be summarised as follows;

5.2.1.1 White lead {2PbCO₃.Pb (OH)₂}

The composition of the Lead Carbonate is 68.9% and Lead Hydroxide is 31.1%. It is used in the manufacture of paints.

Properties:

- Easily applied
- High covering power
- Toxic in nature
- Yellows badly on exposure to the atmosphere
- Soluble in alkali and paints

5.2.1.2 Sublimed white lead (basic sulphate)

The composition of Lead Sulphate is 75%, Lead Oxide 20% and zinc oxide 5%. It is used in the manufacture of paints.

Properties:

- High specific gravity and refractive index
- Slow chalking out of the film producing a rough surface

5.2.1.3 Zinc oxide (ZnO)

The composition of Zinc Oxide is 100%. It is opaque to UV light and thus protects us from UV, prevents chalking.

Properties:

- Brilliantly white having excellent texture
- Causes no discolouration even in contact with CO₂ gas
- More durable in combination with white lead

5.2.1.4 Lithopone

The composition of lithopone is 28.30% zinc oxide and 72.70% barium sulphate. It is widely used for the cold water paints, traffic plants, floor covering and oilcloth industry.

Properties:

- Extremely fine and cheap pigment
- Good hiding power

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• Not as durable as white lead and zinc oxide

5.2.1.5 Titanium dioxide

It consist of TiFeO₃, TiO₂ (iliminite+rutile). It is widely used in paints, in paper and textiles.

Properties:

- High capacity and hiding power
- High oil-absorbing capacity
- Spreading power is almost double as that of white lead
- No tendency of chalking

5.2.2 Blue pigments

Ultramarine Blue and Cobalt Blues are the most widely used blue pigments. The composition, properties and applications of these can be summarised as follows:

5.2.2.1 Ultramarine blue

There are three varieties of ultramarine namely blue, white and green. It is used as bluing in laundering to neutralise the yellowish tone in cotton and linen fabrics. White Ultramarine Blue: Na₅Al₃Si₃SO₁₂, Green Ultramarine Blue: Na₅Al₃Si₂S₂O₁₂, Blue Ultramarine Blue: Na₅Al₃Si₂S₃O₁₂.

Properties:

- Silicate skeleton have a potential influence on the colour
- Colour is because S present is in the form of polysulphide.

5.2.2.2 Cobalt blues

The composition of cobalt blues is 30-35% Co₃O₄ and 65-70% Al₂O_{3.} It is used in the manufacture of blue paints, inks, carbon paper and carbon ribbons. **Properties:**

• Very expensive and are not used in paints for ordinary purposes.

5.2.3 Red pigments

These are one of the oldest-pigments. They are mainly used for inhibiting rusting of iron and steel structures. The composition, properties and applications of these can be summarised as follows:

5.2.3.1 Red lead

It consists of Pb_3O_4 and PbO, used for a primary coat on structural steel and in imparting red colour to the glass for making bangles.

Properties:

- Bright-red powder with a high specific gravity
- Excellent covering power
- Inhibits corrosion

5.2.3.2 Synthetic iron (Fe₃O₄)

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It is widely used in domestic paints, enamels, floors and paints.
Properties:
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- Has a dark brilliant colour
- High covering power and tinting strength

5.2.4 Green pigments

There are two types of commonly used green pigments. The composition, properties and applications of these can be summarised as follows:

5.2.4.1 Chrome green (Cr_2O_3)

It is generally used as green pigments. **Properties:**

- High power of oil absorption.
- It has disadvantages such as lack of brilliancy and opacity

5.2.5 Chromium oxide or guignet's green $[Cr_2O(OH)_4]$

It is used as paint for metal surface and as non-fading green for washable distempers.

Properties:

- Have high covering power
- High corrosion inhibition capacity

5.2.6 Black pigments

They have good tinting strength and as well as high hiding power. The composition, properties and applications of these can be summarised as follows:

5.2.6.1 Natural black oxide

The composition of Fe_2O_3 is 94–95%. It is used in making paints for priming metal.

Properties:

• Oil absorption power is 10–15 kg of linseed oil per 100 kg of Pigment

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5.2.6.2 Precipitated black iron oxide

It is used in cement emulsions and water paints. It has a high hiding power.

5.2.6.3 Carbon black/furnace black

It is used in making waterproof paints. **Properties:**

- Increases the life of paints
- Good tinting strength
- Not affected by light, acids and alkalies

5.2.6.4 Lamp black

It is used in making black pigments. **Properties:**

- Good tinting strength
- Resistant to high temperature

5.2.7 Yellow pigments

The composition, properties and applications of these can be summarised as follows:

5.2.7.1 Ochre

It consists of naturally occurring yellow Fe_2O_3 . It is used in the paint industry. **Properties:**

- Fast to light
- Inert to chemical action

5.2.8 Chrome yellow

It is used in making yellow paints. **Properties:**

- Great opacity
- High brilliance
- High hiding power
- High tinting strength

5.2.9 Toners

Insoluble organic dyes are known as tonners. These can be used as pigments, quite durable and have high colouring power. Various dyes such as para red, Hansa Yellow G (lemon yellow), Hansa Yellow 10G (primrose yellow) etc. have been used as toners in the pigment industry.

5.2.10 Metallic powders as pigments

The powdered form of some metals, as well as some alloys, are used as pigments. Finely powdered aluminium and bronze have been used as pigments in lacquers. Pigments containing finely powdered zinc have been used for protective coatings on iron and steel to protect them from atmospheric corrosion [17–30].

6. Conclusions

This comprehensive chapter on structure and properties of dyes and pigments including some specific applications has been discussed. Moreover, recently the consumers have become very much conscious about the environment, renaissance of eco-friendly products and process like dyeing textiles with natural dyes, which has thus become also important now. Thus, revival of natural dye application on textiles and summary of earlier researches on standardisation of its method of extraction, mordanting, dyeing process variables and even natural finishing, etc. have been elaborated in this chapter. Thus this part has become a unique comprehensive chapter for information on structure and properties of dyes and pigments.

Conflict of interest

There is no conflict of interest.



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