Notes

34

DYES, PAINTS AND PIGMENTS

In the previous lesson you have learnt about polymers which are important industrial products. In this lesson we shall take-up another broad area of chemical industry viz; dyes, paints and pigments. These are organic or inorganic substances which find applications in imparting color to fabrics, leather, buildings, furniture and other objects. Psychologists attach special significance to the choice of colours by a person and to his/her state of mind.

Objectives

After reading this lesson, you will be able to :

- define dyes, paints and pigments;
- write formula or composition of dyes, paints and pigments;
- explain the process of dyeing and classify various dyes;
- differentiate among dyes, paints and pigments;
- classify paints and pigments;
- list various examples of dyes : Indigo, methyl orange, aniline yellow, alizarin and malachite green and etc. and
- list uses of various dyes, paints and pigments.

34.1 Dyes

In the early times the colouring materials were extracted from natural sources like plants and insects. Now a days thousands of such substances are synthesised in factories on a large scale.

Dyes are the organic compounds that are used to impart colour to textiles, foodstuffs, silk, wool and other objects. Dyes are capable of getting fixed to the fabrics/objects permanently and are resistant to the action of water, soap, light, acid, and alkalies.

Every coloured compound cannot be used as a dye. A good dye must have most of the following properties:

1. It must have a suitable colour.
2. It must be able to fix itself or capable of being fixed to the fabric from the solution.
3. When fixed, it must be fast resistant to the action of light, water, soap, detergents, etc. during washing or to the organic solvents during dry cleaning.

34.1.1 Why do dyes or dyed articles appear to have a characteristic colour?

If a molecule absorbs light in the visible region (400 nm to 750 nm) corresponding to green colour, then it will appear violet, which is the complementary colour of green. Similarily, if a dye absorbs blue colour, it will appear yellow which is the complementary colour of blue. Thus, the dyes impart colour to fabric by absorbing the complementary colour.

34.1.2 Constitution of Dyes

The colour of a compound is due to the presence of certain groups containing multiple bonds. These groups which impart colour to a compound are called **chromophores.** Some examples of chromophores are :

$-NO_2$ (Nitro), –N = O (nitroso), –N = N – (azo), quinonoid structures, etc.

At the same time, there are certain groups which they are not chromophores themselves but they deepen the colour when present with coloured compounds. The groups which deepen the colour of a coloured compound are called auxochromes. Some examples of common auxochromes are :

–OH, $-NH_2$, –NHR, $-NR_2$, –Cl, $-CO_2H$, etc.

34.1.3 Classification of Dyes

A large number of dyes are used for various purposes. These are classified on the basis of their

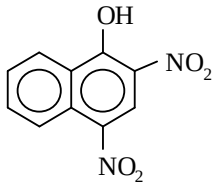
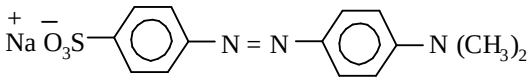
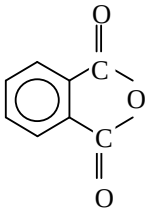
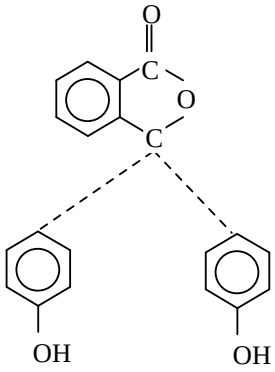
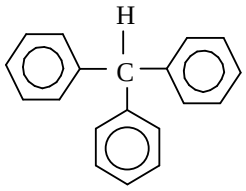
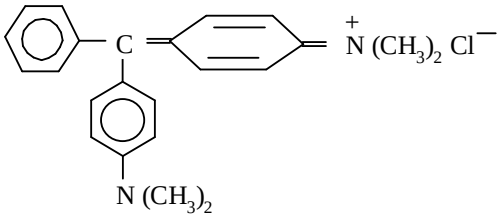
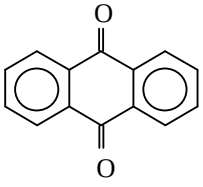
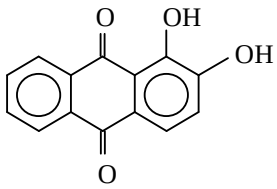
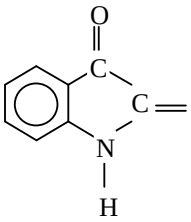
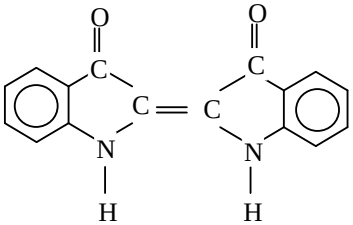
(i) constitution

(ii) application

Classification based on constitution :

Depending upon the **characteristic structural units,** the dyes, are classified as given in Table 34.1 :

Table 34.1 : Classification of some dyes on the basis of their constitution

Dye type	Characteristic Structural unit	Typical examples
(1) Nitro dyes	$-NO_2$	 **Martius yellow (2, 4-dinitro-l-naphthol)**
(2) Azo dyes	–N = N–	 **Methyl orange**
(3) Phthalein dyes		 **Phenolphthalein**
(4) Triphenyl methane		 **Malachite green**
(5) Anthraquinone		 **Alizarin (ruby red)**
(6) Indigoid		 **Indigo**

Intext Questions 34.1

1. Which is the structural unit of Methyl orange?

   .....

2. What is the wavelength range of visible region of spectrum?

   .....

3. What are complementary colours?

   .....

4. How is the structure of a dye related to its colour?

   .....

Classification of Dyes on the basis of their applications.

Dyes are classified into the following types on the basis of their applications.

(i) Acid dyes (ii) Basic dyes

(iii) Direct dyes (iv) Disperse dyes

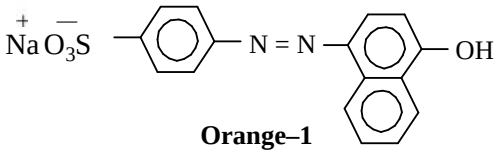
(v) Fibre reactive dyes (vi) Vat dyes

(vii) Insoluble azo dyes (viii) Mordant dyes

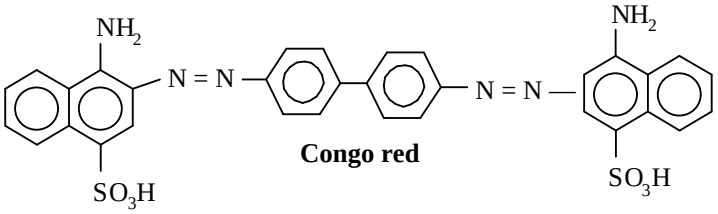
(i) Acid Dyes

These are azodyes used in the form of their sodium salt of sulphonic acid ($-SO_3H$), carboxylic acid (– COOH) or phenol. The dye can be applied to wool, silk and nylon. These do not have much affinity for cotton and therefore, cannot be used to dye cotton.

The common examples of an acid dye are orange – I and congo red.



Orange–1



Congo red

(ii) Basic Dyes

These dyes contain basic groups like ($-NH_2$) group or ($-NR_2$) group therefore these are called basic dyes. These dyes attack the anionic sites present on the fabrics and get attached to them. These are used to dye modified nylons, polyester, wool, cotton, leather, paper, etc.

Aniline yellow, malachite green and crystal violet are the basic dyes.

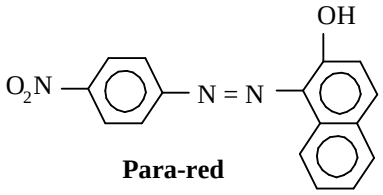
(iii) Direct Dyes

As the name suggest these dyes can be directly applied to the fabrics from their aqueous solution. The direct dyes attach to the fibre by means of hydrogen bonding. These are very effective for dying cotton, wool and rayon.

Martius yellow (Table 34.1) and congo red are the common examples of direct dyes.

(iv) Ingrain dyes

These dyes are very important because over 60% of the dyes used are **azodyes** or ingrain dyes. The fabric to be dyed is soaked in an alkaline solution of phenol or napthol and is then treated with a solution of diazotised amine. These are used for cotton, silk, polyster and nylon. The colour is not very fast because the interaction is only on the surface. For example, para-red is an ingrain dye.



Para-red

(v) Disperse Dyes

These dyes are usually applied in the form of a dispersion of finely divided dye. The dyes are disperesed in a soap solution in the presence of phenol, cresol or benzoic acid. These are used for nylon, polyster and polyacrylonitrile.

Some common examples of disperse dyes are celliton fast pink B and celliton fast blue B

(vi) Reactive dyes

These dyes attach to the fibre themselves by irreversible chemical reactions. These dyes induce fast colour on the fibres which is retained for a longer time. These dyes are used to dye fibres like cotton, wool or silk. Dyes which are drivatives of 2, 4 dichloro – 1, 3, 5 – triazine are important examples of fibre reactive dyes.

(vii) Vat dyes

Vat dyes are the well-known dyes they are insoluble in water and hence cannot be used directly for dying. Therefore, they are reduced to a colourless soluble form (leuco) in large wooden vats with a reducing agent such as an alkaline solution of sodium hydrogensulphite. Under these conditions, the leuco form develops affinity for the cellulose fibre. Then the fabric is exposed to air which oxidises the leuco (colourless) form to coloured form.

Therefore, these dyes are mainly used to dye cotton fibres. Indigo is an important example of this type (Table 34.1).

(viii) Mordant Dyes

These dyes require an additional substance (generally a metal ion) for fixing to the fibre. These are used mainly for dyeing wool. The method involves the precipitation of certain mordant material (binding agent) on the fabrics which then combines with the dye to form an insoluble coloured complex called lake. For acid dyes, metal ions are used as mordants but for basic dyes, tannic acid is used as the mordant. For example, **alizarin is a mordant dye (Table 34.1). It gives a rose red colour with Al^{3+} and a blue colour with Ba^{2+}, a brownish red colour with chromium (Cr^{3+}) and a black violet with iron mordant.**

Intext Questions 34.2

1. How are mordant dyes applied to fabrics?

   .....

2. Give an example of a Vat dye.

   .....

3. Distinguish between acidic and basic dyes?

   .....

4. Why do azo dyes not impart fast colours to fabrics?

   .....

Now we shall discuss about pigments.

34.2 Pigments

Pigments are various organic and inorganic insoluble substances, which are widely used as surface coatings. They are also employed in the ink, plastic, rubber, ceramic, paper and linoleum industries to impart colour. The pigment industry is usually regarded as associated with paints, but in fact it is a separate industry. A large number of pigments are mined or manufactured for the commercial preparation of paints. About 45 year back, white lead [$2Pb\,CO_3 + Pb\,(OH)_2$], Zinc oxide (ZnO) and lithopone ($ZnS + BaSO_4$) were the principal white pigments in use while the coloured pigments consisted of Prussian blue, lead chromates, various iron oxides and a few lake colours. Composition, properties and uses of various pigments will be discussed in the next section.

34.2.1 Classification of Pigments

Pigments are broadly classified into two types :

1. White Pigments
2. Coloured Pigments

White pigments are of various types. Their composition, properties and applications are summerised in Table 34.2 :

Table 34.2 : Composition, properties and uses of some white pigments

S.No	Name of Pigment	Composition	Characteristic Properties	Application or Uses
1.	White lead $2\,PbCO_3.Pb(OH)_2$	$PbCO_3$ = 68.9% $Pb(OH)_2$ = 31.1%	1. Easily applied 2. High covering power 3. Toxic in nature 4. Yellows badly on exposure to atmosphere 5. soluble in alkali and paints	In manufacture of paints.
2.	Sublimed white Lead (Basic sulphate)	$PbSO_4$ = 75% PbO = 20% ZnO = 5%	1. High specific gravity and refractive index. 2. Slow chalking out of the film producing a rough surface.	In manufacture of paints
3.	Zinc oxide (ZnO)	ZnO = 100%	1. Brilliantly white having excellent texture. 2. Causes no discoloration even in contact with CO_2 gas. 3. More durable in combination with white lead.	1. It is opaque to UV light and thus protects from uv. 2. Chalking can be prevented.
4.	Lithopone ($ZnS+BaSO_4$)	ZnS = 28-30% $BaSO_4$ = 72-70%	1. Extremely fine and cheap pigment. 2. Good hiding power 3. Not as durable as white lead and zinc oxide	1. Widely used for cold water paints. 2. Traffic paints. 3. In floor covering and oil cloth industry
5.	Titanium dioxide (TiO_2)	$TiFeO_3$ and TiO_2 iliminite + rutile	1. High opacity and hiding power 2. High Oil absorbing capacity 3. Spreading power is almost double than that of white lead. 4. No tendency of chalking.	1. In paints 2. In Paper and textiles. 3. In other industries.

Blue Pigments

The most widely used blue pigment is ultramarine blue. There are three varieties of ultramarine namely blue, white and green. The comparative study of blue pigments is

given in Table 34.3 :

Table 34.3 : Composition, properties and uses of some blue pigments

S.No	Name of Pigment	Composition	Characteristic Properties	Application/ Uses
1.	Ultramarine Blue	White – $Na_5Al_3Si_3SO_{12}$ Green – $Na_5Al_3Si_2S_2O_{12}$ Blue – $Na_5Al_3Si_2S_3O_{12}$	1. Silicate skeleton have a potential influence on the colour 2. Colour is due to the fact that S present is in the form of polysulphide.	1. Bluing in laundering to neutralize the yellowish tone in cotton and linen fabrics
2.	Cobalt Blues	Co_3O_4 – 30-35% Al_2O_3 – 65 –70%	1. Very expensive and are not used in paints for ordinary purposes.	1. In manufacture of blue paints. 2. In making inks 3. In marking Carbon papers and carbon ribbons.

Red Pigments

Red pigments are one of the oldest-pigments. These are primarily used for inhibiting rusting of iron and steel structures. Different types of red pigments are summerised in Table 34.4

Table 34.4 : Composition, properties and uses of Red Pigments

S.No	Name of Pigment	Composition	Properties	Applications/ uses
1.	Red Lead (Pb_3O_4)	Pb_3O_4 + PbO	1. Bright-red powder with high specific gravity 2. Excellent covering power. 3. Inhibits corrosion	1. For primary coat on structural steel. 2. In imparting red colour to the glass for making bangles.
2.	Synthetic Iron	Fe_3O_4	1. Has dark brilliant colour 2. High covering power and tinting strength	1. Widely used in domestic paints, enamels, floors and paints.

Green Pigments

There are of two types of commonly used green pigments. Their properties, composition and uses are given in Table 34.5 :

Table 34.5 : Composition, properties and uses of Some Green Pigments

S.No	Name of Pigment	Composition	Properties	Applications/ uses
1.	Chrome Green	Cr_2O_3	1. High Power of oil absorption 2. It has disadvantages such as lack of brilliancy and opacity	As green pigments
2.	Chromium oxide or Guignet's Green	$[Cr_2O(OH)_4]$	1. Have high covering power 2. High corrosion inhibition capacity.	1.As Paint for metal surface. 2. As fast non-fading green for washable distempers.

Black Pigments

Black Pigments have good tinting strength as well as high hiding power. The common varieties are discussed in Table 34.6 :

Table 34.6 : Some Black Pigments

S.No	Name of Pigment	Composition	Properties	Applications/Uses
1.	Natural Black Oxide	Fe_2O_3 – 94-95%	1. Oil absorption power is 10-15 kg of linseed oil per 100 kg of Pigment	In making paints for priming metal
2.	Precipitated Black Iron oxide		1. High hiding Power	In cement emulsions and water paints
3.	Carbon Black/ Furnace Black		1. Increases life of paints 2. Good tinting strength. 3. Not affected by light, acids and alkalies	Used in making water proof paints
4.	Lamp Black		1. Good tinting strength 2. Resistant to high temperature	In making black pigments

Yellow Pigments

The common yellow pigments are summerised in Table 34.7 :

Table 34.7 : Some important yellow pigments

1.	Ochre	Naturally occurring yellow Fe_2O_3	Fast to light and inert to chemical action	In paint industry
2.	Chrome yellow		1. Great opacity 2. High brilliance 3. High hiding power 4. High tinting strength	In making yellow paints

Toners

Insoluble organic dyes are known as **toners** and can be used as pigments. They are quite durable and can have high colouring power. For example, para red, Hansa Yellow G (lemon yellow), Hansa yellow 10 G (Primrose yellow), toluidine toner, etc. are the various dyes that have been used as toners in pigment industry.

Metallic Powders as Pigments

The powdered form of some metals as well as some alloys are used as pigments. For example, 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.

Intext Questions 34.3

1. List the green pigments, their composition and uses.

   .....

2. Write names of some blue pigments.

   .....

3. Which pigment is used to inhibit corrosion of iron and steel objects?

   .....

4. Write the composition of white lead.

   .....

5. Which porperty of zinc oxide protects the vehicles?

   .....

34.3 What are Paints?

Paints are stable mechanical mixtures of one or more pigments. The main function of the pigments is to impart the desired colour and to protect the paint film from penetrating

radiation, such as U.V. rays. The pigments and the extenders are suspended in drying oils called **vehicle.** The vehicle or drying oil is a film forming material, to which other ingredients are added in varying amounts. The paint is applied on a metal or wood surface to give it a protective coating. **Driers** promote the process of film formation and hardening. **Thinners** maintain the uniformity of the film by reducing viscosity of the blend.

The important varieties of paints are emulsion paints, latex paints, metallic paints, epoxide resin paints, oil paints, water paints or distempers, etc.

34.3.1 Constituents of Paints

The main constituents of paints are pigments, oil (vehicle) and some other materials to impart various desirable properties.

(1) Pigments

Pigments are the organic or inorganic insoluble substances which are widely used in surface coatings. They protect the film by reflecting the destructive ultra violet light, to strengthen the film.

The important pigments used for making paints are :

(i) White	:	White lead, titanium dioxide, zinc oxide.
(ii) Red	:	Red lead, Iron oxides, cadmium reds
(iii) Blue	:	Cobalt blue, Iron blues, etc.
(iv) Green	:	Chromium oxide, chrome green
(v) Black	:	Carbon black, lamp black, furnace black, etc.
(vi) Metallics	:	Copper powder, zinc dust, aluminium, etc.
(vii) Metal Protective pigments	:	Red lead, blue lead, zinc and basic lead, etc.

(2) Extenders or fillers

The extenders or fillers are the low cost materials. These are added to the paint in order to decrease the cost of the paint. These supplement the pigment in increasing the covering and weathering power of the film. Talc, china clay, gypsum, silica, barite, glass flakes, asbestos and anhydrite, etc. are used as fillers in paints.

(3) Film forming materials

The vehicle or film forming matetrials serve dual purpose in the surface coating formulations. These are usually called drying and semi–drying oils, depending on the degree of unsaturation. Linseed oil, soyabean oil, tung oil, castor oil, varnishes, casein, fish oil, etc. are used as vehicles or drying oils.

(4) Driers

Certain driers (which are oxygen carriers) have also been used in the paints, in order to accelerate the drying of the film through oxidation and polymerization. Earlier, PbO was

used as a drier, but the **Modern driers** are Co, Mn, Pb, Zn, resinoleate, linoleate and naphthenates, etc.

(5) Thinners or Diluents

Another ingredient, of paint is **thinner.** It is added to the paints to dissolve film forming materials and to dilute concentrated paints for better handling. After adding thinner, the paints may be applied more easily on the surface by brushing, spraying or dipping. **Mineral spirits** and solvents namely **turpentine,** maintains the fluidity of the freshly applied film for reasonable period of time.

(6) Antiskinning Agent

Certain **antiskinning agents** are also added to the paints in order to prevent gelling and skinning of the finished product before application of the paints by brushing, spraying or dipping. Polyhydroxy phenols are usually employed as **antiskinning agents.**

(7) Plasticizers

Plasticizers are added to the paints to provide elasticity to the film and thus prevent cracking of the paint. Chemically, plasticizers are mostly esters. Triphenyl Phosphate, dibutyl phthalate and castor oil etc. are used as **Plasticizers.**

(8) Resins :

Varnishes are used as natural or synthetic resins. Examples of natural resins are copal or resin, while that of synthetic resins are Urea formaldehyde, acrylate, vinyl or silicone resins.

(9) Binders

Binders act to fix the paint on the coated surface and provide tough, tenacious and glossy film on the painted surface.

(10) Other Compounds

Water based paints also require dispersing agents (e.g. Casein), antifoam agents, (e.g. pine oil) and preservative (e.g. chlorophenol).

34.3.2 Paint Removers

The substances or materials which are used to remove various surface coatings or paints are called **paint removers.** Paint removers are either flammable or non-flammable.

Flammable paint removers may be liquid removers, semipaste remover and paste removers. The common **solvents** used for the purpose are alcohols such as methanol, ethanol or propanol. Hydrocarbons (benzene, toluene or xylene), acetone and ethyl acetate are also used as paint removers.

34.3.3 Special Applications of Paints

In addition to provide a thin protective layer, paints are also used for other applications some of the special uses are discussed below :

(a) Paints are extensively used as acid resisting coats.

(b) Oil bound water paints or distempers are widely used for interior decoration of walls.

(c) Coaltar products dissolved in mineral spirits have been used as protective coatings of pipes under the name bituminous paints.

(d) Bottom of ships are protected by antifouling paints which are prepared by mixing iron oxide, mercuric oxide and copper resinate dispersed in tung oil.

(e) A paint with **damp resisting properties** is prepared by mixing paraffin wax, rosin, bitumen and gutta parcha dispersed in tung oil.

Intext Questions 34.4

1. Which constituent of paint is used to decrease the cost of the paint?

   .....

2. List antifouling agents used to prepare marine paints?

   .....

3. Write three properties of emulsion paints.

   .....

4. How can we apply paints on the surfaces?

   .....

What You Have Learnt

- Dyes are coloured compounds used in imparting colour to the textiles, food stuffs, silk, wool and other objects.
- A dye is a coloured organic compound which can absorb light in the visible region of the electromagnetic spectrum (400 nm to 700 nm). The part of the light which is reflected back gives the colour of the dye i.e. complementary to the colour absorbed.
- Dyes are classified on the basis of their structures and on the method of applications.
- Pigments are various organic and inorganic insoluble substances, which are widely used in surface coatings.
- Titanium dioxide is one of the most important white pigment. Carbon black, graphite and lamp black are the chief black pigments, chromium oxide (Cr_2O_3) and Guignet's green are green pigments, Chrome yellow, strontium chromate and barium chromate are yellow pigments.
- Insoluble organic dyes are known as **toners** and can be used as pigments. They are quite durable and have high colouring power.

- Some powdered form of metals as well as alloys have also been used as pigments. Finely powdered zinc has been used for protective coating on iron and steel.
- Paints are stable mechanical mixtures of one or more pigments, extenders fillers, driers, thinners or diluents, lacquers, plasticizers, resins and binders.
- A good quality paint should have good colour, high hiding power and also have proper pigment volume concentration range(PVC) . For exterior house paint the PVC range should be 28-36%.
- Varnishes differ from paints in that they have no pigments and in varnishes a part or whole of the oil is substituted by resin.

Terminal Exercise

1. Give structure and name of a direct dye.
2. Classify dyes on the basis of their structural units.
3 Give a scheme or preparation of phenolphthalein. How does it behave under (a) acidic (b) alkaline conditions?
4. What are mordant dyes? What type of binding forces exist between the dye and the mordant?
5. Write preparation, properties and uses of the following pigments.

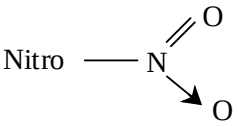
   (i) Zinc oxide

   (ii) Lithopone
6. Describe various components of paints and their significance.
7. List requirements of good paints.

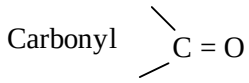
Answers to Intext Questions

34.1

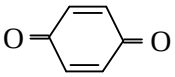
1. – N = N – group
2. The range of visible region of spectrum is [400 nm to 750 nm].
3. A dye is an organic compound which can absorb light in the visible region of the electromagnetic spectrum (400 nm to 750 nm). The part of the light which is reflected back gives the colour of the dye i.e. complementary to the colour absorbed.
4. The structure of a dye is related to its colour due to the presence of certain unsaturated groups (the groups with multiple bonds)



Azoxy $-N=\overset{1}{N}-O$



Azo $-N=N-$



Polyene $-(HC=CH)_n-$

34.2

1. Mordant dyes are used mainly for dyeing of wool. The method involves the precipitation of certain substances (mordant material) on the fabrics which then combine with the dye to form an insoluble coloured complex called lake depending on the kind of mordant used (material designed to bind dye).

2. Indigo

3. Difference between Acid dyes and Basic dyes

Acid dyes	Basic dyes
1. These are azodyes usually sodium salt of $-SO_3H$, – COOH and Phenolic group.	1. These dyes contain ($-NH_2$) group or ($-NR_2$) group as oxochromes
2. The dye can be applied to wool, silk and nylon.	2. These are used to dye modified nylons, polyester, wool, leather etc.
3. Do not have any affinity for cotton.	3. Have affinity for cotton.

4. Because the interaction is only on the surface. The colour goes out on washing.

34.3

1. Green pigments are :

   (a) Chrome green

   (b) Chromium oxide

(a) Chrome green – It is chromium oxide (Cr_2O_3) and has high power of oil absorption. It is used as green pigment, known as **chrome green.**

(b) Chromium oxide – It is also called as Guignet's Green. It is a hydrated chromium

oxide $[Cr_2O(OH)_4]$. It is used as paint for metal surfaces and as a fast non-fading green for washable distempers.

2. (i) Ultramarine Blue

   (ii) Cobalt Blue and Iron Blue

3. Red lead

4. Lead carbonate, 60.2 – 68.9% and lead oxide, 31–39.9%.

5. It is opaque to white light.

34.4

1. Extenders or fillers

2. Zinc oxide, resin (Shellac), driers (Mn lineolate), vehicle (Coal-tar), diluent (pine-oil)

3. (i) Highly durable (ii) Impermeable to dirt

   (iii) resistant to washing

4. (i) Hand-painting or brushing

   (ii) Spraying (iii) dipping

   (iv) Roller coating (v) Tumbling