DEPARTMENT OF TEXTILE ENGINEERING

Course Material

Tex 207: Wet Processing-I

2nd Year 2nd Semester

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Course Content

Technology of Dyeing:

- Elementary concepts of colour and constitution (Chromophore, Chromogene, Auxochrome, Resonance theory)
- Definition of dyestuffs, Pigments and their classifications.
- Commercial dyestuff preparations (Powder, Paste, Lump, Solution and presscake).
- History of dyeing,
- Structure and application of Direct dyes on different fibres
- Structure and application of Acid dyes on different fibres
- Structure and application of Basic dyes on different fibres
- Structure and application of Vat dyes on different fibres

Technology of Printing.

- Flow chart of Printing,
- Thickeners (types of Thickeners)
- Methods and styles of Printing
- Printing processes for different fibres with Direct, Acid, Basic and Vat dyes.

Reference Books

1. ***An Introduction to Textile Coloration: Principles and Practice (2017)***

   -Roger H. Wardman
2. ***Basic Principles of Textile Coloration (2001)***

   -Arthur D Broadbent
3. ***Fundamentals and Practices in Colouration of Textiles 2Ed (2014)***

   -J N Chakraborty
4. ***Handbook of Textile and Industrial Dyeing Vol- I&II (2011)***

   - M. Clark
5. ***Synthetic Dyes (2009)***

   -Gurdeep R. Chatwal
6. ***Textile Printing 2Ed (2003)***

   -Leslie W C Miles

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Chapter-1: Elementary Concept of Color and Chemical Constitution

1.1 What is color?

The psychological sensation which is produced when the light of certain wave length reaches the eye is known as the colour. Thus, colour is dependent on and varies with the nature of the light, illuminating the coloured substances. Total electromagnetic radiations of varying wavelengths which can be categorized:

γ-rays	X-rays	UV	Visible	Infrared Rays	Micro Waves	Radio Waves

VIBGYOR

Violet	Indigo	Blue	Green	Yellow	Orange	Red

The ordinary light consists of electromagnetic radiations of varying wavelengths which can be categorized in three headings:

Part of light	Range of Wave Length
Ultraviolet	100-400 nm
Visible	400-700 nm
Infrared	700-10000 nm

1.2 What color will we see when white light is Incident on a substance?

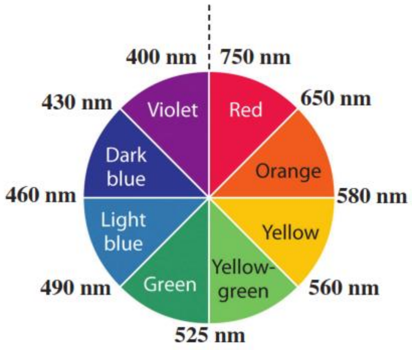
When white light is Incident on a substance, colour is obtained in the following different ways:

i) If the white light is reflected completely, the substance will appear White.
ii) If the white light is absorbed completely, the substance will appear black.
iii) If all the wavelengths of white light are absorbed except a single narrow band which is reflected the colour of the substance will be the colour of the reflected band. For example, if the substance absorbs all wavelengths except one single band say the blue (450 nm) which is reflected, the substance will appear blue.
iv) If only a single band of white light is absorbed, the substance will have the complementary colour of the absorbed band. For instance, blue colour is produced if light of 590 nm (region of yellow colour) is absorbed because the composite of the remaining wave-lengths which are reflected gives the psychological sensation of blue colour. Thus, blue and orange are said to be complementary colors because the absorption of one from white light gives the other. The relation of colour

absorbed and colour visualized with respect to a given range of wavelength is given in Table 1.1.

Table 1.1: Colour absorbed and colour visualized with respect to wavelength regions

Wave length (nm)	**Color absorbed**	**Color Visualized**
400-430	Violet	Yellow-Green
430-460	Dark Blue	Yellow
460-490	Light Blue	Orange
490-525	Green	Red
525-560	Yellow-Green	Violet
560-580	Yellow	Dark Blue
580-650	Orange	Light Blue
650-750	Red	Green

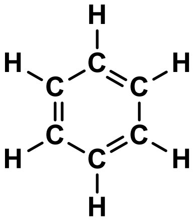


1.3 Is there any relation between colour and chemical constitution?

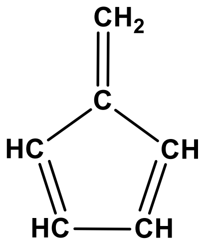
The colour of a compound is related to its chemical constitution. It is evident from the following examples.

i) Benzene is colourless while its isomer fulvene is coloured.

ii) Reduction of coloured organic compounds results in the loss of colour and oxidation of the reduced compounds regenerates the original colour.



Benzene (Colourless)



Fulvene (Coloured)

The relation between colour and chemical constitution of a substance has been explained by different theories which are described as follows:

1. Witt's Theory (1876)
2. Armstrong's Theory (1888)
3. Nietzki's Theory (1889)
4. Baeyer's Theory (1907)
5. Watson's Theory (1914)

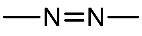
1.4 How is the relation between colour and chemical constitution explained by Witt's theory?

Our modern understanding about colour & colour constitution was first reported by a German Chemist **O. K. Witt** in **1876.** According to this theory, there existed a relationship between colour and chemical constitution of a compound and further a dye is made up of two parts namely

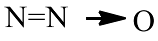
1. Chromophore
2. Auxochrome

Chromophore

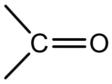
The colour usually appears in an organic compound if it contains **certain unsaturated groups**. **Witt** called these groups as the **chromophores** (***Greek chroma-colour,*** and ***phoros- bearing).*** For example, **diazomethane** contains the **unsaturated** group, **azo group**, and is, therefore, **yellow** in colour. The complete molecule that contains the chromophore is known as ***chromogen*** while the side chains are known as auxochrome.



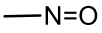
Azo



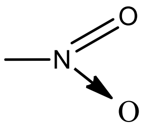
Azoxy



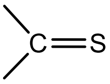
Carbonyl



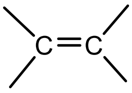
Nitroso



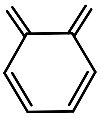
Nitro



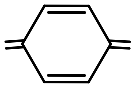
Thiocarbonyl



Ethylenic



o-quinonoid



p-quinonoid

Types of Chromophores

The chromophores listed in the previous table are of two types:

1. Independent chromophores

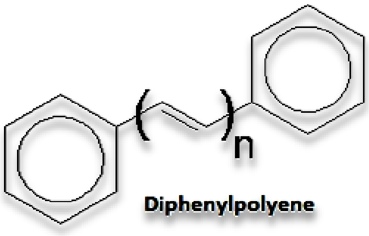
This type includes such chromophores when a ***single chromophore is sufficient to impart colour*** to the compound. Examples of such chromophores are

-N=O, –NO_2, -N=N-, -N=N→O, p-quinonoid etc.

2. Dependent Chromophores:

This type includes such chromophores when ***more than one chromophore is required to impart colour.*** Examples of such chromophores are =C=O & =C=C=. For example, $CH_2=CH_2$ is colourless while $CH_3(CH_2)_6CH_3$ is yellow.

In case of Diphenylpolyene,



Diphenylpolyene

When n = 0, I or 2, the compound is colourless.

n= 3, the compound becomes yellow and

n is further increased, the colour gets deepened, i.e. when n=5, the colour is orange,

n=7, the colour is copper-bronze and

n=11, the colour is violet-black.

Auxochromes

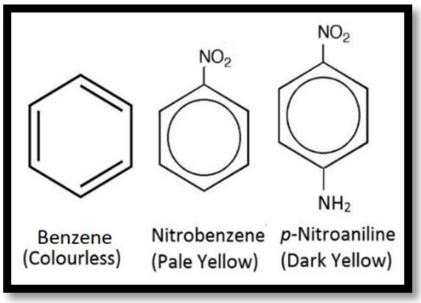
Witt pointed out that the presence of **certain groups** in a chromogen leads to a **deepening of the colour** although these groups are **not chromophores** themselves and **do not impart colour** to the compound when present without the chromophore. Witt called these groups as auxochromes which can influences the colour..

Table: Some Typical Auxochromes

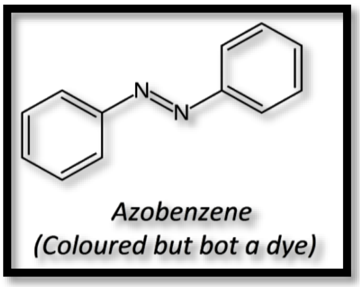
Name	Group	Name	Group
Amino	$-NH_2$	Chloro	$-Cl$
Methylamino	$-NHCH_3$	Methyl	$-CH_3$
Dimethyl amino	$-N(CH_3)_2$	Methoxy	$-OCH_3$
Hydroxy	$-OH$	Cyano	$-CN$
Sulphonic acid	$-SO_3H$	Accetyl	$-COCO_3$
Carboxylic acid	$-COOH$	Acctamado	$-CONH_2$

Function of Auxochromes

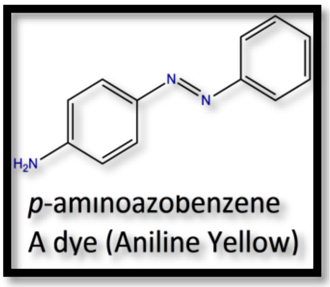
1. They increase the ***intensive of the colour,*** This is illustrated by the following example
2. They **make the chromogen a dye** by fixing it to the fabric or the material to be dyed either by **association or by salt formation.** The fixing of the dye to the fibre is generally due to the formation of chemical bond between the fibre and the auxochrome. This is best illustrated by the following example:



Benzene (Colourless) Nitrobenzene (Pale Yellow) *p*-Nitroaniline (Dark Yellow)



Azobenzene
(Coloured but bot a dye)



p-aminoazobenzene
A dye (Aniline Yellow)

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 colour.

Types of Auxochromes

Auxochromes are mainly of two types:

i) Bathochromic auxochromes:

These are the groups which **increase the depth of the colour**. These shift the **absorption maxima** from the **violet towards the red** and thereby bring about the **deepening** of the colour. It is called **red shift**. When the **hydrogen atoms** in an amino group **$-NH_2$** are replaced by **$-NHR$ or $–NR_2$**, a **bathochromic effect** is produced.

ii) Hypsochromic auxochromes:

These are the groups which **decrease the depth** of the colour. These shift the **absorption maxima** from the **red to violet** and these results in the **fading of the colour**.

It is called **blue shift.** A **hypsochromic effect** is observed when **-OH or -NH2** group of a dye is replaced by **$-OCOCH_3$** or **$-NHCOCH_3$** group respectively.

Witt's theory has been proved extremely useful **empirical guide** in developing many of the dyes.

1.5 What are the modern theories to explain the relation between colour and chemical constituents?

Two theoretical approaches were developed to explain the relation between colour and chemical constituents namely -

i) Valence Bond (resonance)
ii) Molecular Orbital (MO) methods

These theories are based upon the following concepts:

- Absorption of radiation by molecules
- Dipole Moment

Absorption of radiation by molecules

A compound appears coloured if it selectively absorbs light in the visible region and reflects the light of wavelengths in the rest of the visible region. The amount of light energy absorbed in the visible spectrum is the only responsible factor for the shade of the colour.

The main function of the absorbed energy is to raise the molecule from the ground state energy, E_o to the excited state, E_1 and the difference of energy, ΔE is the quantum of energy given by quantum theory equation.

$$\Delta E = E_1 - E_0 = h\nu = h\frac{C}{\lambda}$$

Where,

h = Planck's constant

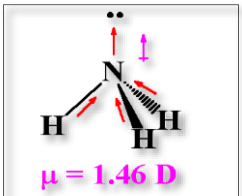
c = Velocity of light

λ= Wavelength of the absorbed radiation

The amount of energy absorbed, ΔE, depends upon the structural configuration of that dye. In other words, ΔE depends upon how tightly the electrons are bound in the bonds and accordingly the absorption will occur in UV or a particular region of visible range.

For instance, if the electron of a molecule are tightly bound as in saturated compounds, no light of visible region will be absorbed but only light of ultraviolet region will be absorbed and hence the compound will appear colourless.

If the electrons of a molecule are loosely bound as in saturated compounds, the absorption may occur in the visible region and the substance will then appear coloured. For a coloured region and the substance will then appear coloured.



Dipole Moment of NH_3

Dipole Moment

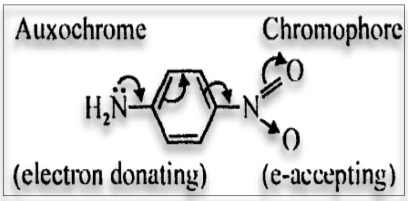
It is the **polarity of a chemical bond** within a molecule. Its value ranges **0-11 Debyes.** The dipole moment plays a significant role in the **transition**

of the molecule because a molecule can **absorb light** only if its **dipole moment changes.**

For example, the ***more symmetrical the molecule*, *the smaller is the probability of transition dipole*** and, therefore, the light is absorbed by the molecule very slowly.

Similarly, it is shown that ***the greater the transition dipole, the greater is the absorption of intensity.*** Thus, if the group, which is introduced in the molecule, **decreases the symmetry of the molecule,** the **transition dipole and, therefore, the intensity of the absorbed light will also be increased.**

1.6 How does Valence Bond (resonance) theory explain the relation between colour and chemical constituent?



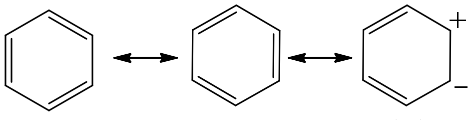
- In resonance theory, the **chromophore** is considered as an **electron accepting group** and auxochrome as **an electron donating group.** When they are **conjugated** through double bonds (usually benzenoid systems) then **electrons move from auxochrome to chromophore.**
- This **increases the resonance** and also causes the **change in dipole moment.** Hence intensity of colour is increased. The **dipole moment** changes as a result of **oscillation of electron pairs.** The following order has been observed for the ease of excitation of different groups.

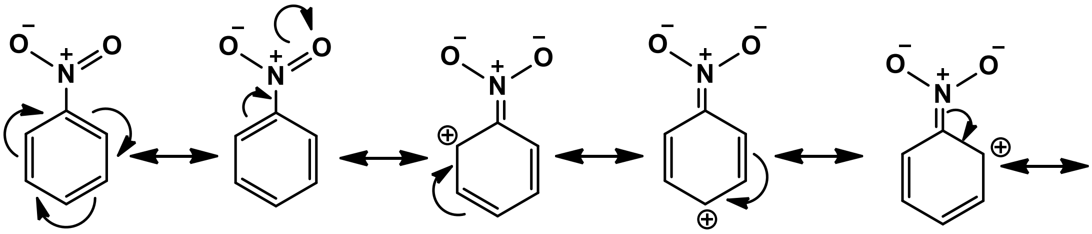
$$N = O > C = S > N = N > C = O > C = N > C = C$$

The colour deepens in the opposite direction.

1.7 Why is Benzene colourless but *nitrobenzene pale yellow*?

In benzene, **two major structures** contributing to its resonance hybrid are the two **Kekule structures** (I and II). In addition, a number of **charged canonical structures of type III** may be written but they **contribute relatively little** to either ground or excited state and thus benzene **absorbs in the ultraviolet region.** Also, the benzene molecule is **symmetrical** and, therefore, the **absorption is weak.**


(I) (II) (III)

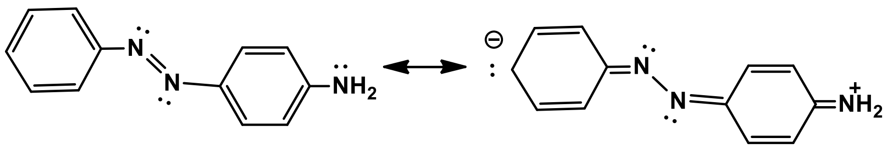


In nitrobenzene, **charged structures** contribute much more than in the case of benzene and, therefore, the **absorption is shifted to longer wavelength (blue),** thereby producing a **pale yellow colour** which is the complementary colour of the blue band. Also, the **intensity of the absorption is increased** in nitrobenzene due to the **loss of symmetry of the molecule.**

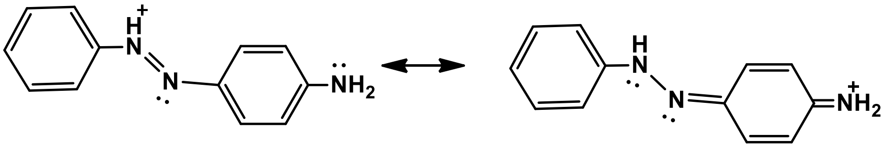
1.8 Why is p-aminoazobenzene yellow in alkaline medium but violet in acidic solution?

In alkaline or natural medium, there is only one changed structure contributing to the resonance structure. It absorbs in the blue region and hence, shows yellow colour.

In acidic medium, it gets protonated and both the resonance structures are charged. Therefore, it absorbs at a longer wavelength in the yellow-green region and shows violet colour.

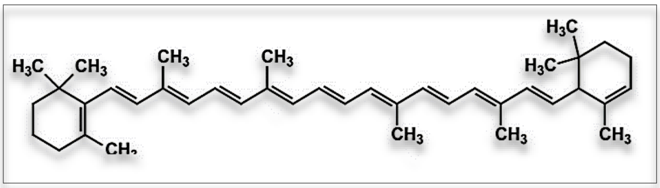


Yellow (Alkaline or neutral medium)



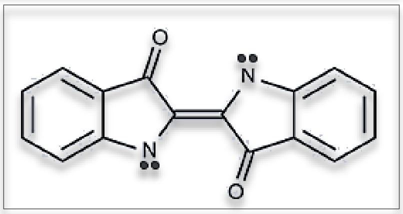
Violet (Acdic medium)

1.9 The colour of carrot and indigo dye



β–carotene:

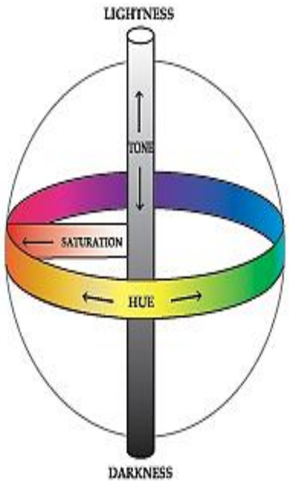
It absorbs light of 470 nm & its complementary colour is orange.



Indigo:

It absorbs light of 610 nm (in ethanol) & its complementary colour is blue.

1.10 By which attributes is colour expressed?

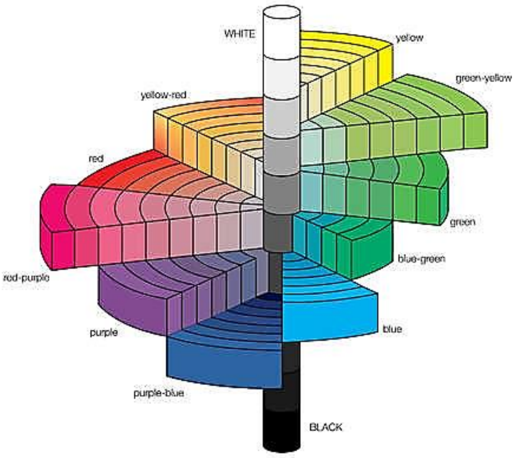


Munsell in 1905 proposed three psychological attributes (hue, value, and chroma) that have become generally accepted for object colours. Wyszecki (1981) put forward the empirical evidence of three attributes as being sufficient for an observer with normal colour vision to describe any perceived colour. His terms for the three attributes were hue, lightness, and chroma or saturtion.

Hue- The term hue is defined as an 'attribute of visual perception according to which an area appears to be similar to one of the colours red, yellow, green, and blue etc.

Lightness- Lightness is that attribute of colour which distinguishes light colours to dark colours and whites from greys and blacks.

Chroma- It describes the purity of colour and is zero for whites, grey and black but increases to a maximum with vivid colours such as those shown by flowers or highly chromatic pigment or dye.



Chapter-2: Introduction to Dyes

2.1 What is colorant?

A colorant is a substance which imparts colour to a particular substrate (e.g. textile material, paper and leather). As such, colorants include dyes and pigments, both of which are coloured materials that are (usually) employed for imparting colour to an object, but which differ in their physical form and, thereby, the manner in which they are applied to a substrate.

2.2 What is dye or dyestuff?

It is a substance, usually organic, which is designed to be absorbed or adsorbed by, made to react with, or deposited within a substrate in order to impart colour to that substrate with, or deposited within a substrate in order to impart colour to that substrate with some degree of permanence. All the dyes may not necessarily be coloured substances. Therefore, optical brighteners or whiteners which may be called white dyes may be included in the term dye.

2.3 ETAD defines dyes as

Dyes are intensely colored or fluorescent organic substances only, which impart color to a substrate by selective absorption of light. They 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.

[ETAD – The Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers. Further information on ETAD is available from their web site http://www.etad.com]

2.4 What is Pigment?

Pigment is a substance in particulate form which is substantially insoluble in a medium, but which can be mechanically dispersed in this medium to modify its colour and/or light scattering properties.

2.5 CPMA defines pigments as

Pigments are 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. Pigments are usually dispersed in vehicles or substrates for application, as for instance in the manufacture or inks, paints, plastics or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process.

[CPMA – Color Pigment Manufacturers Association, Inc. Further information on CPMA is available from their web site http://www.pigments.org/cms1]

2.6 Similarities between Dye and Pigment

- Dye and pigment are two types of compounds which can give a color to a material.
- Therefore, they are known as colorants.
- Also, both can be either natural or synthetic.
- They have various applications in the textile industry, printing, painting, candle making, etc.

2.7 Difference between Dye and Pigment[2]

Criterion	Dye	Pigment
Definition	A dye refers to an intensely colored or fluorescent organic substance, which imparts color to a substrate by selective absorption of light.	Pigment refers to the colored, black, white or fluorescent particulate organic or inorganic solids, usually insoluble in, and essentially physically and chemically unaffected by, the substrate in which they are incorporated.
Type of Compounds	Most dyes are organic.	Pigments can be either organic or inorganic.
Auxochrome Groups	Auxochrome groups can be present in dyes.	No auxochrome groups are present in pigments.
Size	A dye particle is very small.	Pigment particle is comparatively large.
Solubility	Dyes are soluble in water.	Pigments are not soluble in water and many solvents.
Transparency	Dyes are more transparent.	Pigments are comparatively less transparent.
Affinity	Dyes have a direct affinity to the material.	Pigments have no direct affinity to the material.
Binding Agents	Dyes do not require binding agents to be attached with the substrate.	Pigments require binding agents to be fixed with the substrate..

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[1] https://colour-index.com/definitions-of-a-dye-and-a-pigment

[2] https://pediaa.com/what-is-the-difference-between-dye-and-pigment/

Diffusion	Dyes diffuse in the fabric.	Pigments diffuse on the fabric.
Structural change during Application	The structure of dyes temporary alters during the application process	The structure of pigments does not alter during the application process.
Colour Fastness to wash	Poor to Excellent ranges of dyes are available.	Pigment produces Very Good to excellent fastness.
Colour Fastness to light	Low rating.	High rating.

2.8 What are the requisites to consider a colour compound as a true dye?

All coloured substances are not dyes. However, the requisites of a true dye are as follows:

1) It must have a stable colour.
2) It should not undergo structural changes readily·
3) It must be able to attach itself to material from solution or to be capable to fix on it.
4) It must be soluble in water or must form a stable and good dispersion in water. Alternatively, it must be soluble in the medium other than water. However, it is to be remembered that the pickup of the dye from the medium should he good.
5) The substrate to be dyed must have a natural affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion. If necessary in the presence of auxiliary substances under suitable conditions of concentration temperature and pH.
6) When a dye is fixed to a substrate, it must be fast to washing, dry cleaning, perspiration, light, heat and other agencies.

2.9 How are the colourants classified?

The current 4th edition of Colour Index (at present completely online : www.colour-index.org) which is jointly published by the Society of Dyers and Colourist (SDC) and the American Association of Textile Chemists and Colorists (AATCC), Contains over 34,500 individual products under 11,570 Colour Index™ Generic Names; over 1500 dyes are produced in commercial quantities (in 2014 CE)[3].

It classify colorants according to:

1. Application, for the user seeking information on commercial products, dyeing properties, etc. Colourants are classified mainly in terms of application and in terms of chemical class.

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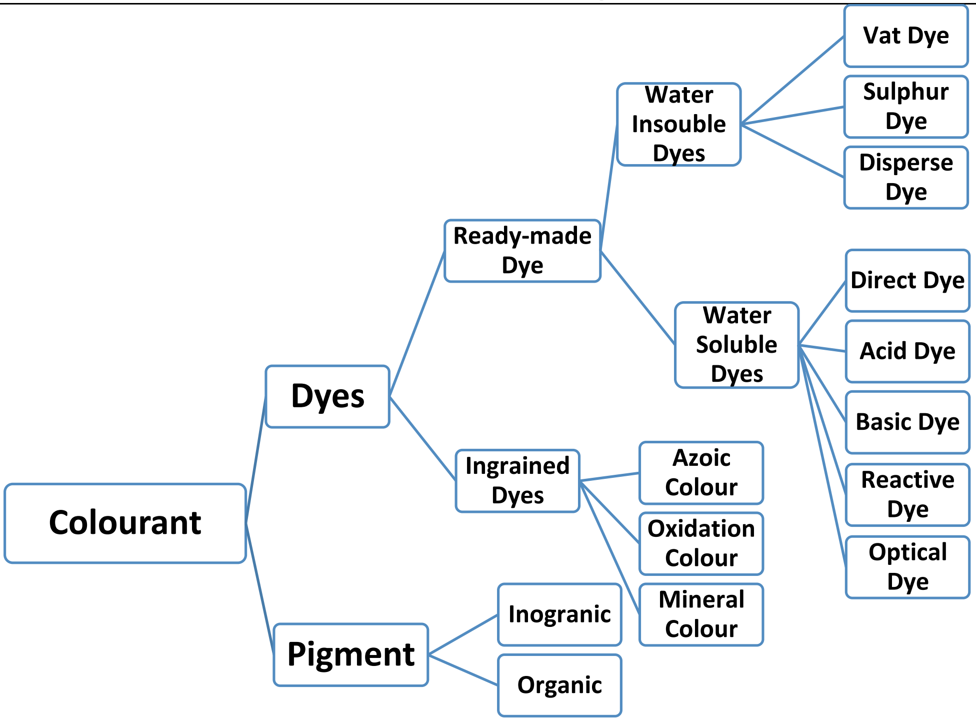
[3] https://colour-index.com/colour-index-generic-name

2. Constitution, for the chemist requiring information on chemical structure, preparative methods, etc.

In the *Colour Index*, the **27 chemical classes of dye** are distributed unequally between the **19 application classes of dye**.

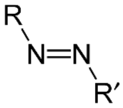
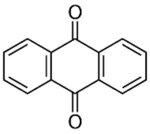
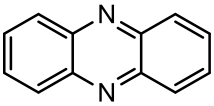
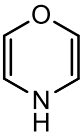
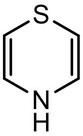
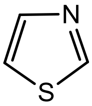
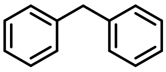
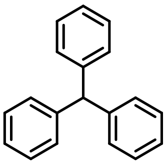
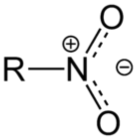
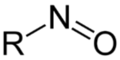
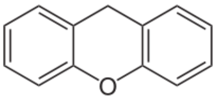
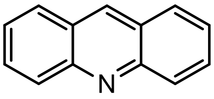
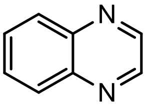
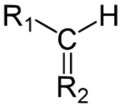
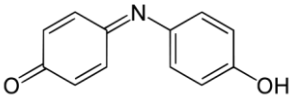
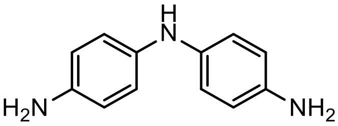
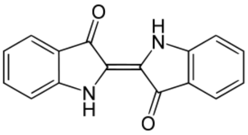
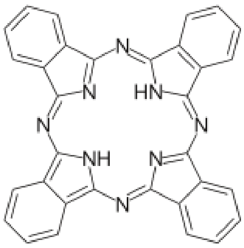
2.10 Classification of colourants of according to application



Besides, Colour Index application classes have some more dye types mainly for non-textile application.

- Food dyes
- Leather dyes
- Natural dyes
- Solvent dyes

2.11 Classification of colourants of according to Chemical Constitution

1. Azo

2. Anthraquinone

3. Azine

4. Oxazine

5. Thiazine

6. Thiazole

7. Diphenylmethane

8. Triphenylmethane

9. Nitro

10. Nitroso

11. Xanthene

12. Acridine

13. Quinoline

14. Methine

15. Indophenol

16. Indamine

17. Indigoid

18. Phthalocyanine

19. Sulphur Complex Mixed Structure
20. Stilbene Complex Mixed Structure

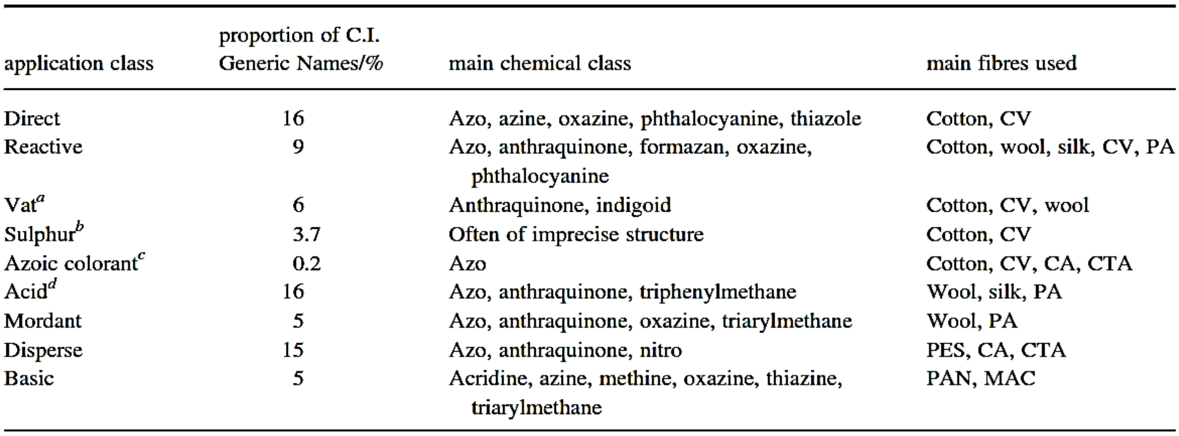
The seven most populous chemical classes in descending order, namely

- Azo ~59%,
- Anthraquinone ~18%,
- Sulphur ~4%,
- Phthalocyanine 2%,
- Azine ~1.8%,
- Xanthene ~1.6% and

- Triarylmethane ~1.6%, collectively account for ~88% of the colorants listed.

However, the majority of the 27 chemical classes of dye, which are (unequally) distributed between the 19 application classes of dye, were discovered in the nineteenth century (exceptions include metal-complex dyes, disperse dyes and reactive dyes) when only natural fibres and a small number of regenerated fibres were available. The subsequent introduction of man-made and, especially, synthetic fibres that occurred during the twentieth century was accompanied by the introduction of comparatively few new classes of dye

2.12 Main application and chemical classes of dyes used on textiles



application class	proportion of C.I. Generic Names/%	main chemical class	main fibres used
Direct	16	Azo, azine, oxazine, phthalocyanine, thiazole	Cotton, CV
Reactive	9	Azo, anthraquinone, formazan, oxazine, phthalocyanine	Cotton, wool, silk, CV, PA
Vat[a]	6	Anthraquinone, indigoid	Cotton, CV, wool
Sulphur[b]	3.7	Often of imprecise structure	Cotton, CV
Azoic colorant[c]	0.2	Azo	Cotton, CV, CA, CTA
Acid[d]	16	Azo, anthraquinone, triphenylmethane	Wool, silk, PA
Mordant	5	Azo, anthraquinone, oxazine, triarylmethane	Wool, PA
Disperse	15	Azo, anthraquinone, nitro	PES, CA, CTA
Basic	5	Acridine, azine, methine, oxazine, thiazine, triarylmethane	PAN, MAC

Each dye class possesses both merits and demerits in that each of the five application classes of dye that can be used on cellulosic fibres varies in terms of, for instance,

- Ease of application (high: reactive dyes; low: vat dyes),
- Colour gamut (wide: reactive dyes; restricted: sulphur dyes),
- Shades obtainable (dullish: sulphur dyes; bright: azoic colorants),
- Need for additional after-treatment agent (direct dyes),
- Dye cost (high: vat dyes; low: sulphur dyes) and
- Fastness properties (high: vat dyes; low: direct dyes),

All of which, in turn, are a consequence of the chemical structure of the dye.

2.13 In which forms commercial dyes are available?

Dyes are available in the market in different forms, such as –

☐ Fine powders

☐ Granular

☐ Aqueous paste

☐ Liquid solution or

☐ Dispersions

2.14 Are the commercial dyes 100% pure?

Commercial dyes are not available in pure form, they usually contain various other chemicals besides the principal dyestuff. These include –

- Buffers (e.g. Acetates, Phosphates),
- Non-Electrolytes (e.g. Dextrin),
- Neutral Salts (e.g. Na_2SO_4, Nacl),
- Alkalis (e.g. Na_2CO_3, Nahco),
- Antifoams (e.g. Glycols),
- Anti-Dusting Agents (E.G. Mineral Oils),
- Antifreeze (e.g. Glycols),
- Thickeners (e.g. Carboxymethyl Cellulose) And
- Dispersants (e.g.. Lignin Sulfonates)

The type and amount of formulation additive employed depends on the type of dye (e.g. acid dyes and reactive dyes) and intended application method (exhaust, continuous, etc.). The additives, which are intended to impart a variety of effects to a given dye formulation such as adjustment of tinctorial strength, pH and viscosity, will be present in both the dyebath and fibre at the end of dyeing.

2.15 Commercial Names of the Dyes

A wide range of dyes are manufactured and are marketed throughout the world under a variety of trade names. Such trade names typically comprise three components,

i) The first being a *brand/trade name*, which often denotes the manufacturer and the intended area of application,
ii) The second is the *colour* of the dyeing obtained on the intended textile substrate and,
iii) Finally, a series of code letters and numbers that define more precisely the shade characteristics and other properties of the dye.

Example

***NOVASOL®* Orange 3R (Generic Name: *CI Vat Orange 23*)**

NOVASOL *= Brand name of vat dye manufactured by Huntsman*

Orange *= Hue of the dye*

3R *= Shade characteristic e.g. 3 times Reddish.*

Within a given dye range, it is common for members to be of the same colour (e.g. red) but of different shade (e.g. yellowish, bluish, etc.), this being reflected in commercial dye names often including code letters and numbers (e.g. *2R*, *5G*, etc.) to indicate the shade characteristics of a dye.

However, even though a dye with the same C.I. Generic Name may be available from different dye producers marketed under different commercial/brand names, the dyes may not be exactly equivalent, since samples of ostensibly the same dye from different makers may well vary in terms of purity, the presence of shading components,

physical form (e.g. particle size in the cases of disperse dyes and vat dyes) and may contain differing amounts of additives, such as diluents, dispersants and buffers..

Not all dyes have a C.I. Generic Name, not simply because ***one has not been assigned,*** but often because the dye may be ***a mixture of several coloured constituents***, as is the case with many *black and navy dyes.*

2.16 Global Dye Consumption

Although precise figures for global dye production are unavailable in the public domain, a realistic estimate can be obtained by assuming that an average of 2% on mass of fibre (*omf*) dye is used for textile coloration.

Accordingly, as world textile fibre demand in 2012 was 78.9×10^6 T of which PES fibres accounted for ~50% (43.3×10^6 T) and cotton fibres ~35% (23.4×10^6 T), global dye production can be assumed to be 1.6×10^6 T, of which the majority (≥ 50%) can be ascribed to that of disperse dyes and reactive dyes.

2.17 What dyes were used in textile dyeing before the discovery of synthetic dyes?

Dyes have been used since ancient times for colouring and printing fabrics. Until the middle of last century most of the dyes were derived from plants or animal sources by long and elaborate processes. Among these the following deserve special mention:

- **Indigo -** It is one of the earliest natural dyes and it originated in Indian subcontinent. Then the use of this dye spread to Egypt. Indigo occurs in the *indigo-ferae* species of plants
- **Tyran Purple -** It is a natural dye which originated in the ancient city of Tyre in Phoenicia. This dye was extracted from certain kinds of shell-fish. However, at that time the dye was so expensive that it was called Royal purple.
- **Alizarin -** It is extracted from the roots of madder plant.
- Cohineal **-** It was extracted from the insect coccus Cacti which is found mainly in South America and Mexico.
- **Logwood -**It is the only natural dye which is still isolated on a large scale from the wood of the tree Haematoxylon Campechianum. It is cultivated and also grows wild in the Central America.

2.18 What are the major limitations of Natural Dyes

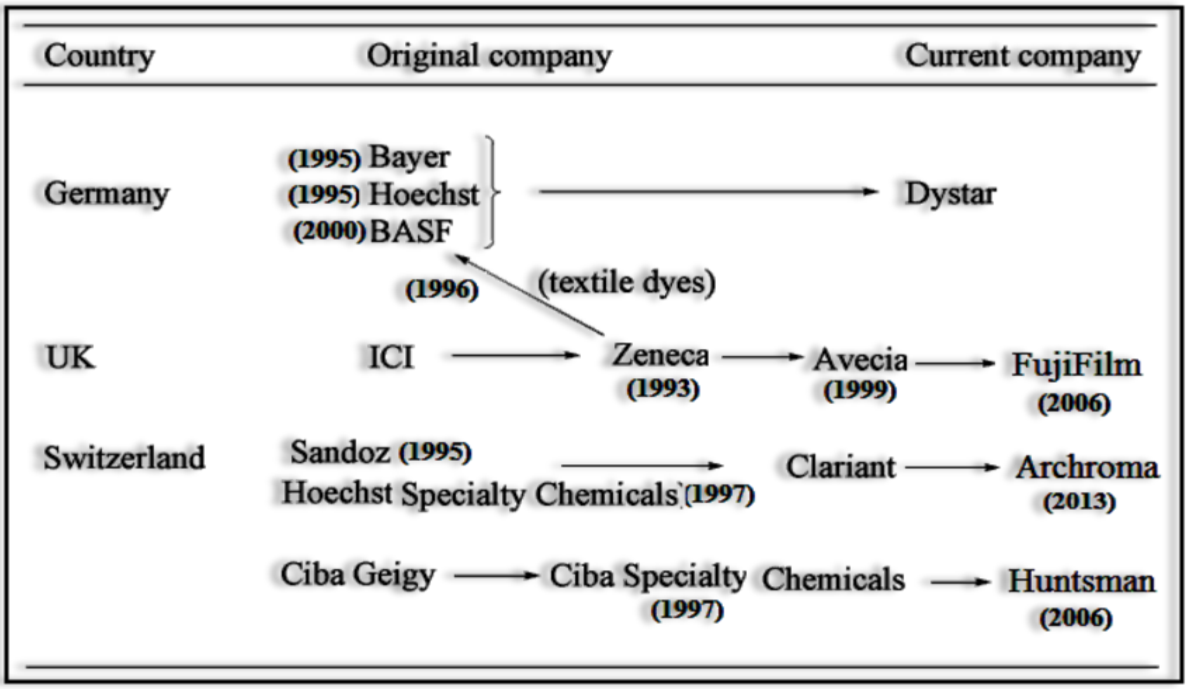
A large number of natural dyes were thus extensively used earlier. However, the preparation of dyes by extraction has number of limitations.

1) The extractions are unsuitable for large scale preparation as they are labourious and time consuming.
2) Only a small amount of the dye can be obtained by processing a large amount of the animal or vegetable matter. Hence they were invariably expensive.
3) The natural dyes are not pure and lack uniformity of quality. Further their fastness properties were not good and they fades in light. Thus only a handful of natural dyes are still extracted and used.

2.19 List chronological Development of dyestuffs

Dye Type	First Dye name	Discoverer	Year
Basic dye	Mauve or aniline	W.H. Perkin	1856
	Fuchine	François-Emmanuel Verguin	1859
Acid dye	Alkali Blue	E.C. Nicholson	1862
Vat dye	Alizarin	Carl Graebe and Carl Theodore Liebermann	1868
	Indigo	Adolf von Baeyer (discovered structure and synthesize indigo)	1880
	Indantharene	Rene Bohn	1901
Direct dye	Congo Red	Paul *Böttiger*	1884
Sulphur dye		Raymond Vidal	1893
Azoic dye		Zitscher & Laske	1911
Disperse dye	A simple azo dye		1920
Phthalocyanine		Linstead & Diesbach	1928-1929
Reactive dye	Procion	Rattee & Stephen (commercialized ICI)	1956

2.20 Transformation of Dyestuff Industries



Chapter-3: General Aspects of Textile Dyeing

3.1 What is dyeing?

The application and fixing a dye to a substrate, normally with the intention of obtaining an even distribution throughout the substrate is called dyeing.

3.2 What are the factors to select a dye for the colouration of textiles?

There are numerous factors involved in the selection of dyes for colouring a fabric in a particular shade. Some of these are:

1) The types of fibres present.
2) The form of the textile material and the degree of levelness required.
3) Fastness properties required for any subsequent manufacturing processes and for the particular end-use.
4) The dyeing method to be used, the overall cost, and the machinery available.
5) The actual colour requested by the customer.

3.3 By which forms can textile materials be dyed?

Textile materials can be dyed at various stages of their manufacture. The particular stage at which coloration is achieved depends on many factors such as-

- The manufacturing process involved
- Processing costs
- End use
- Fastness requirements.

Dyeing of textile materials can be proceeded by the following ways-

1. Mass Colouration / gel dyeing
2. Fibre dyeing
3. Yarn dyeing
4. Fabric dyeing
5. Garment dyeing

3.4 By which methods textile materials can be dyed?

These can conveniently be divided into two groups depending on the general application procedure employed.

1. Immersion (Exhaustion) Methods

The whole of the textile material is accessible to all the dye liquor throughout the dyeing process. The degree of levelness and penetration achieved are mainly controlled by

- Uniform conditions of pH
- Proper temperature
- Proper and uniform electrolyte concentration
- Adequate and uniform rate of dye liquor-fiber agitation

2. Impregnation-Fixation Methods

The material is first impregnated with a solution or dispersion of the dye which, ideally, remains deposited mechanically within the material until the dye is fixed within the fiber during the subsequent fixation stage. This dyeing method is utilized in -

1) Semicontinuous processes.
2) Continuous processes.

3.5 What are the stages to transfer dye from the solution to a fibre?

Essentially, dyeing comprises three stages:

1) Dye molecules, in either solution or dispersion, are transferred through an aqueous, non-aqueous or vapour phase, in which the dye resides, to the surface of the textile fibre;
2) Dye molecules are then adsorbed on the fibre surface;
3) The dye molecules diffuse from the surface to the interior of the fibre.

The transfer of dye particle into a fibre is a very complex process and numerous mathematical models are derived to explain the dyeing mechanism. The simplest concept of the dyeing mechanism is -

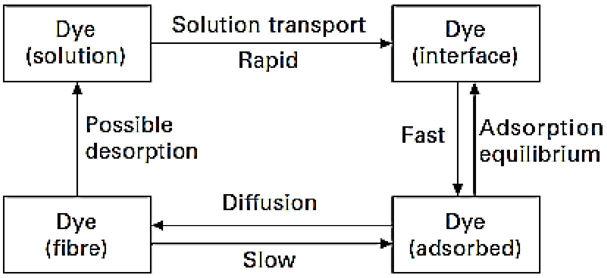


Figure: Dye transfer from the solution into a fibre

- **Adsorption**

Generally, adsorption refers to the accumulation of solute molecules (e.g. dye molecules) at an interface (e.g. solid/liquid and liquid/liquid, such as fibre/dyebath). Adsorption arises due to forces of interaction operating between the adsorbate (i.e. the dye molecule) and the adsorbent surface (i.e. the textile fibre).

- **Absorption**

Absorption is the a phenomenon in which a species from one phase becomes evenly distributed throughout another phase.

- **Sorption**

Sorption is the physical and chemical process by which substance becomes attached to another. The term sorption covers both ad- and ab-sorption.

- **Desorption**

It is a phenomenon whereby a substance is released from or through a surface. The process is the opposite of sorption (that is, either adsorption or absorption).

- **Substantivity**

The term substantivity describes the attraction between a dye and a fibre that results in the preferential adsorption of the dye onto the fibre, when dye and fibre are brought into contact.

- **Affinity**

The quantitative expression of substantivity. It is expressed in units of Joules/mole. Use of this term in a qualitative sense, synonymous with substantivity, is deprecated.

3.6 Terms used in direct exhaust dyeing

- **Exhaustion**

The amount of dye adsorbed by a textile substrate during dyeing is commonly referred to as *exhaustion* and is usually expressed as a proportion (%) of the amount of dye present at the start of dyeing. As the amount of a substance is often measured by its mass, then units for the amounts of dye in the fibre and solution would be mg, g, kg, etc.

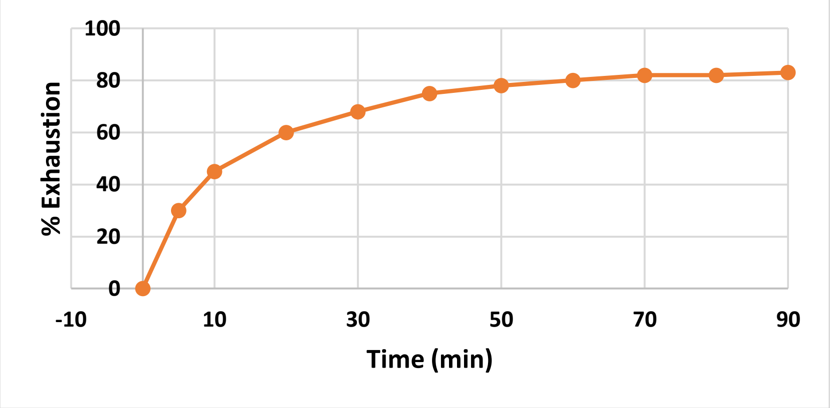
$$\text{\% Exhaustion (\%E)} = \frac{\text{Amount of dye in fibre at end of dyeing}}{\text{Amount of dye in dyebath at start of dyeing}} \text{ x } 100$$

$$\%\text{E} = \frac{C_0 - C_t}{C_0} \times 100\%$$

C_0 = Initial Concentration of dyebath.

C_t = Concentration of dyebath at the end of dyeing.

When the extent of exhaustion of a dyebath, expressed as a percentage of the original amount of dye in the dyebath, $\%E$, is plotted as a function of time of dyeing, t, curves of the general type shown in Figure are obtained.



- **Rate of Dyeing**

The rate at which a dye is absorbed by a substrate under specific conditions. It may be expressed quantitatively in several ways, such as the weight of dye absorbed in unit time or the time taken for the substrate to absorb a given fraction of the amount of dye which it will absorb at equilibrium.

- **Dye Migration**

The movement of dye or pigment from one part of a material to another is call dye migration.

- **Dye Strike**

The rate of dye uptake by a substrate during the initial stages of dyeing is referred to as dye strike. A high strike (aka rapid strike) often results in initial unlevel dyeing (aka non-uniform dyeing or uneven dyeing).

- **Dye compatibility**

One of the dyer’s major objectives is to produce goods having the exact shade desired by the client. This usually requires the use of a mixture of dyes, often a mixture of red, blue and yellow. These should all be dyes with about the same rate of dyeing. They should have very similar rates of exhaustion when used in mixtures under the given dyeing conditions. If the dyes do not have approximately equal dyeing rates, the hue will be constantly changing from that of the more rapidly absorbed dyes towards that of the more slowly absorbed ones that remain in the dyebath longer.

- **Dye Fixation**

The term *dye fixation* describes the proportion of the dye which has been applied to the fibre during the dyeing stage that remains in the substrate at the end of subsequent processing (e.g. rinsing and wash-off). In this context, fixation is expressed as a %, relative to the amount of dye originally applied.

$$\%\ \text{Dye fixation} = \frac{\text{Amount of dye in fibre at end of processing (dyeing/rinse/wash-off/etc.)}}{\text{Amount of dye in fibre at end of dyeing stage}} \times 100$$

- **Amounts of dye / Shade%**

The amounts of dyes used to produce the colour desired are usually expressed as a percentage of the weight of the dry material, and abbreviated as % owf, or % dye on the weight of fibre. In dyeing industry, it is often called as shade%. Thus, 1.00 kg of dye used to colour 100 kg of cloth corresponds to a 1.00% dyeing or 1% shade. Colour reproducibility depends upon accurate weighing of both the goods and the dyes.

  - With increasing amounts of absorbed dyes, the colour of the goods obviously becomes deeper, but also usually duller, and often with a slight change in hue.
  - Deep shades frequently have lower fastness to wet treatments and rubbing than pale shades produced with the same dyes.
  - On the other hand, deeper dyeings have higher light fastness.

- **Colour Yield**

The colour yield is the depth of colour of a dyeing per unit amount of dye in the material. Dyehouse laboratories often determine the relative colour yields of comparable dyes to evaluate their cost effectiveness.

- **Dye saturation value of fibres**

The maximum quantity of a dye which can be absorbed by a substrate under defined condition. Knowledge of saturation value of a fibre is important, keeping in view the maximum shade depth that can be produced on it.

- **Liquor-to-goods ratio / Material-to-Liquor Ratio (M:L)**

The liquor-to-goods ratio, or simply the liquor ratio, gives the weight of the bath solution relative to the weight of the material being dyed. If a piece of textile weighing ‘y’ g is to be dyed at a liquor ratio of 1: 5, volume of water would be ‘5y’ ml. Many newer dyeing machines operate with lower liquor ratios in order to minimise the consumption of energy for heating the water. An increase in the liquor ratio causes -

- A decrease in the degree of exhaustion, under the given conditions, and therefore a decrease in the depth of colour of the dyeing.
- The more consumption of chemicals added during dyeing if these are required at a specific concentration.

- **Colour Fastness**

Dyed textile materials are routinely exposed to variety of *agencies* (e.g. light, perspiration and water) during use, as a result of which the dyed substrate may undergo a change in hue, lightness and/or chroma owing to degradation of the dye within the substrate. The resistance of colour of a textile material against these agencies is called its colour fastness.

- **Dyeing Auxiliaries**

Virtually every dye–fibre system involves the use of additional productswhich are added to dyebaths, in order to promote dyeings of the desired quality (levelness, fastness, hue, colour strength, etc.). It is called dyeing auxiliaries. Such materials range from simple chemicals such as electrolytes (e.g. NaCl or Na_2SO_4) to proprietary chemical products such as *levelling agents*, *anti-creasing agents* and *anti-frosting agents*. In some cases, for example the use of reducing agents in the application of the leuco form of vat or sulphur dyes, the auxiliary is an essential, integral part of the dyeing process.

The 11th edition of the *International Textile Auxiliaries Buyer's Guide* lists over 5,500 commercial products based on 400–600 active components in which the auxiliaries are classified on the basis of functional use according to TEGEWA[4] nomenclature.

- **Wash-Off**

A consequence of incomplete dye fixation (i.e. not all of the dye that has been applied during dyeing will be physically and/or chemically retained by the fibre at the end of dyeing) is that dyed materials are routinely subjected to an aqueous treatment to achieve the desired colour, depth of shade, etc., and also to ensure that vagrant dye molecules do not impair the fastness of the dyeings during use. Such treatments are generically referred to as wash-off and typically comprise multiple rinses with water, often in the presence of alkali or specific auxiliaries.

3.7 What are general process sequences of continuous dyeing?

Most continuous dyeing processes can be divided into four stages:

1) Dye application by padding;
2) Dye fixation, usually in hot air or steam;
3) Washing-off of unfixed dye and auxiliary chemicals;
4) Drying, usually on steam-heated cylinders.

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[4] TEGEWA was established in 1951 in Wiesbaden, the name being an amalgam of TExtilhilfsmittel (textile auxiliaries), GErbstoffe (tanning agents) and WAschrohstoffe (detergent raw materials).

- **Wet Pick-Up**

The weight of dye solution retained per 100 g of dry fabric. It should be high enough that there is sufficient solution to adequately wet the fibres and yarns and allow the dye to uniformly reach the fibre surfaces, but not so high that there is excessive migration on drying. The minimum wet pick-up is usually around 55–60% for cotton/polyester materials, 60–70% for cotton, and higher for fabrics of the more absorbent viscose.

A 70.0% wet pick-up of a dye solution containing 1.80% of dye =70 x 1.80/100 = 1.26 % dye owf.

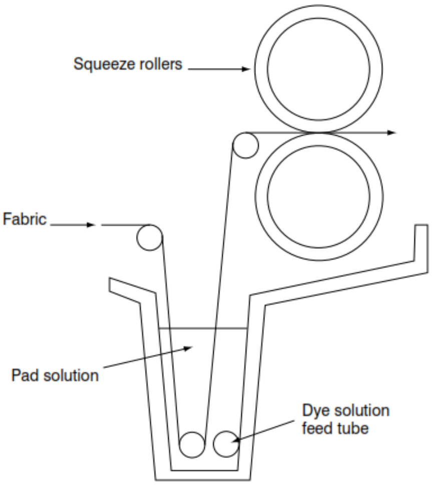


Fig.: Schematic of a Padder

$$\text{Amount of dye}\left(\frac{\text{g dye}}{100\,\text{g fibre}}\right) = \text{Wet pick-up}\left(\frac{\text{g soln}}{100\,\text{g fibre}}\right) \times \text{Dye concn}\left(\frac{\text{g dye}}{\text{g soln}}\right)$$

Chapter-4: Acid dyes and their application

4.1 What is acid dye?

The term ‘acid dye’ derives from the presence in the dye molecule of one or more **sulphonic acid or other acidic groups which** is, those water-soluble, anionic dyes and are applied from acidic (pH 2.0–6.0) to neutral dyebath. The principle fibres to which they are applied are wool, other animal fibres, silk and polyamide.

4.2 Properties of acid dye

i) Since these are sold as a sodium salt, therefore, these form a large anion in the aqueous medium. So these dyes are anionic in nature.
ii) Acid dyes are used for dyeing protein fibers. The main protein fibers used for which acid dyes are used are wool, angora, cashmere and silk. Apart these, milk protein fibers like Silk Latte, Soya Protein, etc., can also be used.
iii) These are applied from a strongly acidic to neutral pH bath.
iv) These dyes have no affinity for cotton cellulose’s, hence not suitable for cellulosics.
v) These dyes combine with the fiber by hydrogen bonds, Vander Waals forces or through ionic linkages.
vi) Overall wash fastness is poor although light fastness is quite good.

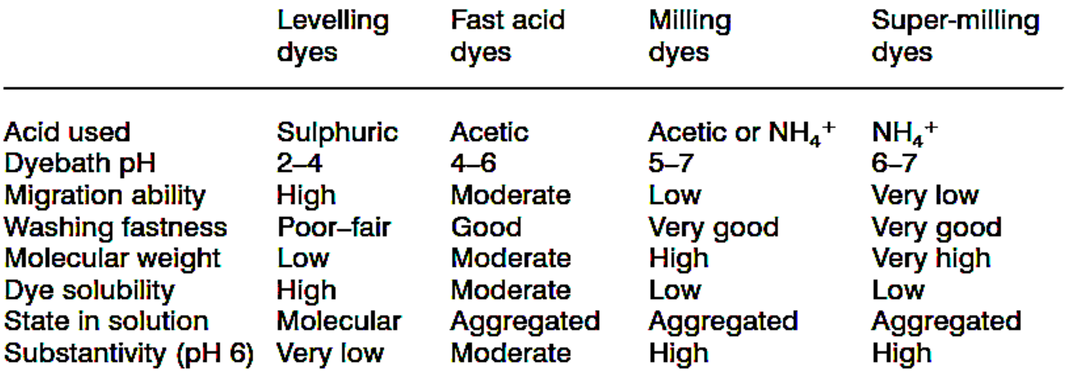
4.3 Classification of acid dyes according to dyeing characteristics

Dyeing characteristics of acid dyes allow them to be categorised into the following four types:

1. Level dyeing or equalising dyes
2. Fast acid dyes
3. Milling acid dyes
4. Super-milling acid dyes.

The molecular weight and degree of sulphonation of the dye molecule determine the dyeing behaviour such as the pH of dyeing, migration ability to dyeing and their washing fastness.

Table: Characteristics of various types of acid dyes



	Levelling dyes	Fast acid dyes	Milling dyes	Super-milling dyes
Acid used	Sulphuric	Acetic	Acetic or NH_4^+	NH_4^+
Dyebath pH	2–4	4–6	5–7	6–7
Migration ability	High	Moderate	Low	Very low
Washing fastness	Poor–fair	Good	Very good	Very good
Molecular weight	Low	Moderate	High	Very high
Dye solubility	High	Moderate	Low	Low
State in solution	Molecular	Aggregated	Aggregated	Aggregated
Substantivity (pH 6)	Very low	Moderate	High	High

4.4 Mechanism of wool dyeing with acid dye

i) Formation of zwitter ion in wool polymer in water

When wool is immersed in water, a proton (H^+) – attached to the carboxylic group at one end of wool – is transferred to $-NH_2$ group at the other end of the macromolecules so that the two ends of wool chain acquire opposite electrical charges and the resulting ion is called:

$$H_2N–W–COOH \xrightarrow{H_2O} H_3N^+–W–COO^-$$

ii) Formation cationised wool in the acidic bath

On addition of acid in bath containing wool with zwitter ions, some of the negatively charged carboxylate ions ($-COO^-$) take up proton – released by acid – into solution and are transformed to electrically neutral carboxylic acid groups ($-COOH$). At the same time, the acid anions, released from acid are absorbed by the positively charged amino ends of keratin macromolecules.

$$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$$

$$H_3N^+–W–COO^- + H^+\ CH_3COO^- \leftrightarrow H_3N^+\ CH_3COO^-–W–COOH$$

iii) Formation of ionic bond between cationised wool and acid dye

Cationic nature of wool increases with increase in time of acid treatment with generation of more and more positive sites ($-NH_3^+$) in wool through absorption of excess acid. When an acid dye (R–SONa) is added to this bath containing cationised wool, the dye anion is attached with cation of wool through electrostatic force with liberation of salt.

$$H_3N^+\ CH_3COO^-\ –W–COOH + R–SO_3^- + Na^+ \rightarrow R–SO_3^-\ H_3N^+–W–COOH + CH_3COONa$$

Some of the groups present in the dye are bound to wool by H-bonds too. Since the dye anion is held on the protein molecules more strongly than the acetate anion, the acetate ions taken up by the positive sites prior to addition of dye are continuously replaced by dye anions. As dyeing proceeds, transfer of different ions from solution to wool and from wool to solution takes place.

4.5 Influence of dyeing parameters

1. Effect of electrolyte

In case of strong acid dyes, electrolyte act as retarding or levelling agent

- Electrolytes act mainly as retarding or levelling agent for strong acid dyes.

$$CH_3COO^-H_3N^+–W–COOH + R–SO_3Na \leftrightarrow RSO_3^-\ H_3N^+–W–COOH + CH_3COONa$$

- Dyeing proceeds with elimination of CH_3COONa. At the initial stages of dyeing– due to higher attraction between cation of fibre and anion of dye – more and more salt will be liberated due to faster attachment developing chances of uneven dyeing.

- A levelled shade can only be produced through reduction in the formation of salt by adding excess salt in bath at the start of dyeing to ensure backward process – stripping – higher the concentration of salt added, higher is the rate of stripping.
- In other words, excess of salt enhances stripping and acts as a retarding or levelling agent.

<u>In case of super-milling acid dye, electrolyte enhance dye adsorption</u>

- For super-milling dyes, which are often applied from a neutral bath, salt plays opposite effect (similar effect as dyeing of cellulose with direct dyes), i.e., salt promotes dye uptake on protein fibres by reducing zeta potential.
- Wool probably acquires a negative electrical potential in neutral solutions, which normally repels the negatively charged acid dye anions present in dye bath.
- Presence of an electrolyte reduces this surface negative charge difference between dye and fibre through absorption of positive sodium ions – released from salt.

2. Effect of acid

Levelling and milling acid dyes are not taken up by protein fibre unless acid is added to bath. As stated earlier, immersion of protein fibre in water transfers the terminal H atom from –COOH and at another end the $–NH_2$ group is protonated. During this process, carboxylic ion is formed at one end of fibre (COO^-) while amine ion (NH_3^+) at the other making the fibre oppositely charged (zwitter ion).

$$H_2N\text{–}W\text{–}COOH \xrightarrow{H_2O} H_3N^+\text{–}W\text{–}COO^-$$

Addition of acid makes the fibre cationic in nature through attachment of H atom of acid to the COO^- ion making it COOH again.

$$CH_3COOH \leftrightarrow H^+ + CH_3COO^-$$
$$H_3N^+\text{–}W\text{–}COO^- + H^+\ CH_3COO^- \leftrightarrow H_3N^+\ CH_3COO^-\text{–}W\text{–}COOH$$

Absence of acid in bath, marked by pH at or above 7.0 will cause repulsion of more dye anions with little dye uptake.

3. Effect of temperature

Acid dyes added to bath can attach themselves with cationic site of fibre through replacement of anion released by acid (CH_3COO^-) which remains attached with the cationic site of fibre.

$$H_3N^+\ CH_3COO^-\ \text{–}W\text{–}\ COOH + R - SO_3^- + Na^+ \rightarrow$$
$$R\text{–}SO_3^-\ H_3N^+\ \text{–}W\text{–}COOH + CH_3COONa$$

This replacement is not possible at room temperature but it is possible only when the bath is heated up causing acceleration of dye molecules to generate the required momentum. Efficient dyeing results are obtained if dyeing is started at about 40°C, raised slowly to boil and dyeing is further carried out at boil for desired time; slow rise in temperature causes replacement of CH_3COO^- ions at a specific rate avoiding unlevelled dyeing. Acid dyes are not transferred from bath to fibre below 39°C, beyond this temperature rate of adsorption increases and the trend varies from one type of dye to other. Milling acid dyes have a minimum temperature of exhaustion at 60°C, but at 70°C, transfer of dye is fast. Super-milling dyes cause level dyeing only at boil.

4.6 Renowned Commercial Acid dyes

Brand Name	Manufacturer
Nylosan	Archroma (Former Clariant)
Lanasyn	Archroma (Former Clariant)
Optilan	Archroma (Former Clariant)
Supralan	Dystar (Former Bayer)
Telon	Dystar (Former Bayer)
Tectilon	Huntsman (Former Ciba)
Erionyl	Huntsman (Former Ciba)

Chapter-5: Direct dyes and their application

5.1 Why direct dye is named so?

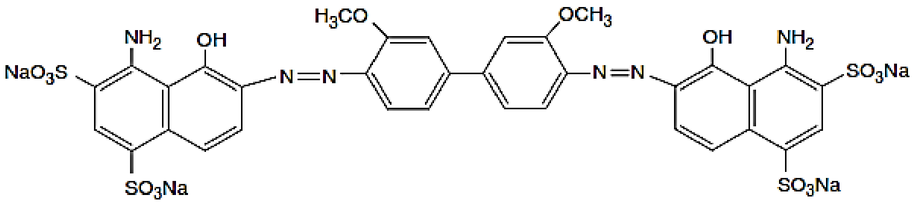
Historically, in order to dye cotton with the dyes available, it was necessary to treat the fabric with a mordant that would ‘fix’ the dye within the fibres. When direct dyes were introduced, they could be applied to cellulosic fibres by a simple one-bath process (i.e. directly) in the absence of a mordant. For this reason they were called ‘direct’ dyes.

5.2 Properties of direct dye

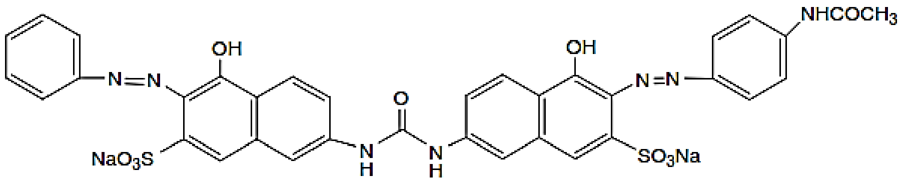
i) All direct dyes are soluble in water, but some of them are more soluble in a weak alkaline medium.
ii) Their solubility also increases considerably with liquor temperature.
iii) Direct dyes are capable of dyeing cellulose, protein and polyamide fibre without preliminary mordanting. However, the application in cotton is most wide.
iv) They are available in full range of hue but do not have color brilliance.
v) Direct dyes on cotton have poor wash fastness, this can somewhat be improved by various after treatments on the fibre.
vi) Their light fastness on cellulosic fibres varies from poor to fairly good, though some copper complex dyes have very good light fastness.

5.3 What is general chemical structure of direct dye?

Direct dyes generally conform to the formula Y_1–N-N–X–N-N–Y_2-, and typical examples are:



C.I. Direct Blue 1



C.I. Direct Orange 25

5.4 What are the differences between direct dye and acid dye?

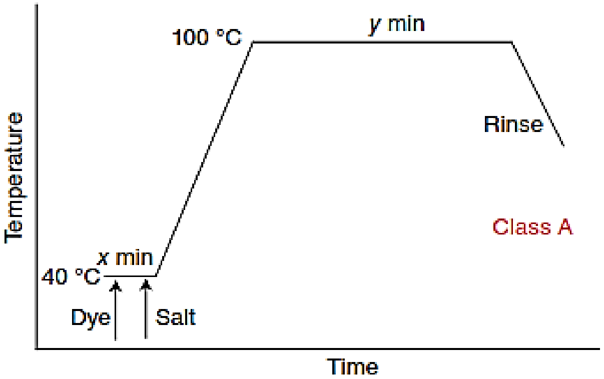
- The molecules of direct dyes are similar in structure to those of acid dyes, but they are larger, that is, they generally have higher molecular weights.
- Another important distinction between direct and acid dyes is in molecular shape. Whilst acid dyes with bulky structural shapes can diffuse successfully into protein

fibres, it is necessary for direct dyes to have long, narrow planar structural shapes, so they can penetrate the more highly crystalline cellulosic fibres.

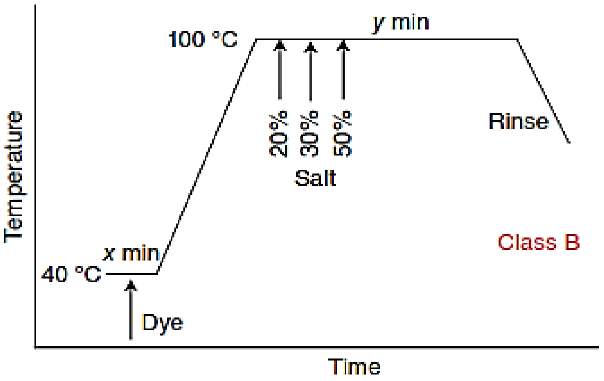
5.5 How are the direct dye classified?

Direct dyes are classified into three classes according to the effect of changes in electrolyte concentration and dyebath temperature on their dyeing properties. The three groups of the SDC classification are the following:

1) Class A (*self-levelling* dyes) contains those dyes that can be applied easily, with electrolyte present from the start of dyeing. They are often used for the shading of faster dyes in hot dyebaths.



2) Class B (*salt-controllable* dyes) contains those dyes for which the rate of addition of electrolyte throughout the dyeing process must be regulated in order to control dyeing.



3) Class C (*temperature-controllable* dye) contains those dyes for which regulation of both the rate of increase of dyebath temperature and the addition of electrolyte are essential for adequate control. Dyes in this class all possess very high substantivity, even in the presence of only small amounts of salt. Because of their marked additional dependence on the dyebath temperature.

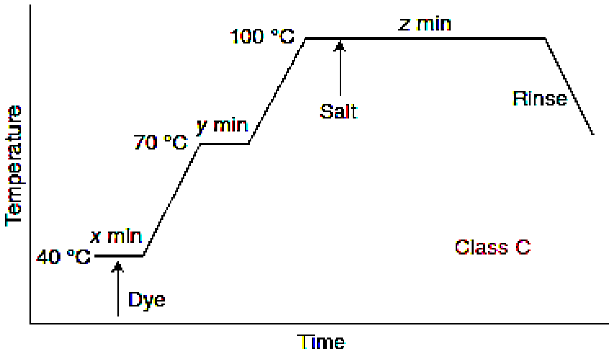


Figure: Typical dyeing profiles for the three classes of direct dyes.

5.6 Typical recipe and conditions of direct dyeing

Dye : x%

T R Oil : just little to make paste

Na_2CO_3: a trace

Salt : 50 g/l

Temperature : room temperature to boil

Time : 2–3 hours

5.7 Which bond is form in case of dyeing cellulose with direct dyes?

The dyes have an inherent substantivity for cellulosic fibres, their attachment being through both

- ***Hydrogen bonds -*** this bonding capability is aided by their long flat molecular shape that enables them to lie along a cellulose chain in register with the –OH groups of the fibre.
- **Van der Waals forces-** the large molecular size increases the opportunity for van der Waals forces to form.

5.8 What is the Mechanism of dyeing cellulose with direct dye?

- Cellulose acquires negative charge on its immersion in water while dye molecules also split to release dye anion in bath.
- Initially few dye anions are absorbed on the surface of fibre but later on most of these are repelled out from the surface due to huge negative potential difference (zeta potential) and further dyeing ceases.
- Addition of electrolyte reduces the zeta potential and promotes absorption by releasing sodium cation which gets attached with dye.
- Sodium salt of dye molecules deposited on the fibre surface slowly diffuse inside water swollen cellulose matrix and places itself alongside the polymer chain with H-bond and Van der Waals forces in the way as shown in Fig.
- Application of heat facilitates breaking of dye aggregates as well as reduces zeta potential.

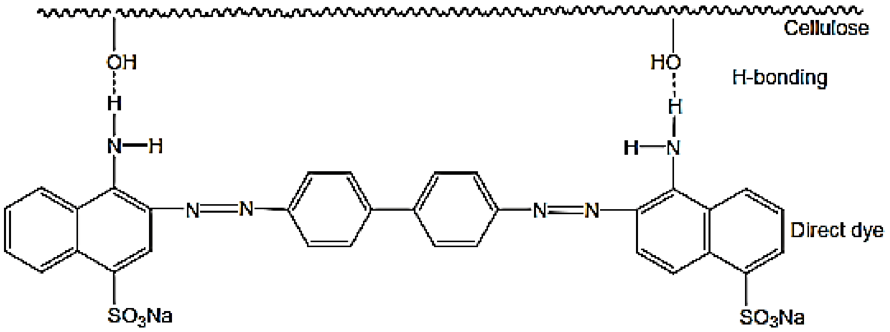


Figure: Attachment of Congo Red with cellulose

5.9 What is the Mechanism of dyeing Jute with direct dye?

- Jute is composed of cellulose, hemicellulose, lignin and fats. Before dyeing, pretreatment is imparted with mild alkali. Application of strong alkali attacks hemicellulose.
- Jute is a cheaper fibre and retains more amorphous region than cotton and it contains hemicellulose; so –OH groups show enhanced affinity for direct dye.
- Method of application is same as that with cotton. Dye uptake is also more than that on cotton for a given dye concentration requiring less dye for a specific shade.

5.10 What is the Mechanism of dyeing protein fibres with direct dye?

- Protein fibres like wool and silk, even nylon possess $-NH_2$ and $-COOH$ groups on terminal ends of polymer chain. Direct dyes can react with these $-NH_2$ groups to form ionic bonds.
- When wool or silk is dipped in acidic bath, $-NH_2$ groups are protonated to form $-NH_3^+$ and dye anions (DSO^-) react with $-NH_3^+$ groups to establish ionic bonds.
- Dyeing rate is so high that electrolyte is added at the start of dyeing to retard dye uptake to form levelled shades. Direct dyes produce fast but dull shades on wool and silk.

Protein fibre (P) $\rightarrow -NH_2-P-COOH \rightarrow NH_3^+-P-COO^- \rightarrow NH_3^+-P-COOH$

Dye $\rightarrow DSO_3Na \rightarrow DSO_3^- + Na^+$

Fixation $\rightarrow NH_3^+-P-COOH + DSO_3^- \rightarrow DSO_3^-\ NH_3^+-P-COOH$

5.11 What are the factors influencing dye uptake in case of direct dyeing?

- **Influence of temperature**

To get maximum dye uptake, rate of heating should be slower with more time for exhaustion; even a lower constant temperature for prolonged time is adequate for that.

- **Effect of pH**

Application of a trace of alkali is required to ensure complete solubilisation of dye; concentration must be too little otherwise exhaustion of dyebath will be poor but with a better levelled shade.

Increase in alkalinity of bath lowers substantivity of dye because of the higher negative potential of both dye and fibre causing more repulsion between these two (higher zeta potential), showing lesser dye uptake. Hence, concentration of Na_2CO_3 must be kept at too lower side.

- **Role of electrolyte**

Addition of electrolyte promotes dye uptake through reduction in zeta potential and promotes substantivity of dye. It also promotes formation of dye aggregates inside the fibre and improves wash fastness.

- **Influence of liquor ratio**

Higher the effective concentration of dye in bath, higher will be the dye uptake. This implies that a lower liquor ratio is more effective for efficient dyeing. Increase in liquor ratio will produce lighter shades and vice versa

- **Time of dyeing**

A slower rate of heating and increase in time of dyeing for a given dye concentration will affect higher dye uptake. If rate of heating is high, lower will be the time to reach to the equilibrium absorption with lower dye uptake and vice versa.

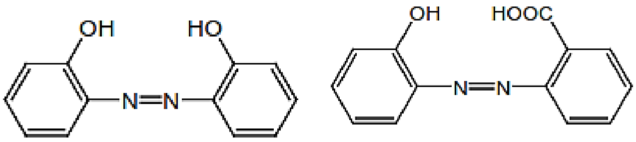
5.12 How can the wet fastness of cellulosic fibre dyed with direct dyed be improved?

Fibres dyed with direct dyes can be after-treated to improve their fastness to wet treatments by increasing the molecular weight of the dye and rendering it less soluble in water. However, this after-treatment can cause a decrease in light fastness. Different methods are available to improve the wet fastness, the most used being:

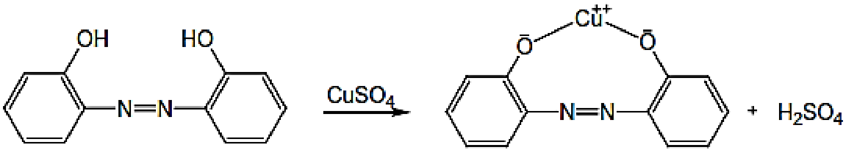
1. Metal complex formation
2. The use of cationic fixing agents

1. Formation of a Metal Complex

In this method, the dyed fibres are treated at 70–80°C with a copper salt to form a dye–metal complex. For the method to work though the dye needs to contain a O–O′ hydroxy, O–O′ carboxyl and O–hydroxy O′carboxyl groups shown in structure, so it is not applicable to all direct dyes.



If the direct dye possesses O–O′ dihydroxy azo-based structure, its attachment with metal takes place as follows:



Various metal salts of copper, iron, nickel and chromium may be used in this after-treatment either alone or in combination based on cost and hue to be developed but generally salts of copper and chromium are preferred, i.e., $CuSO_4$ and $K_2Cr_2O_7$.

Although there is an improvement in the light fastness, the treatment gives a change in the hue, but the effect is not always permanent and de-metallisation can occur gradually during repeated domestic washing. Another disadvantage of this process is the use of copper salts, because discharge of these metal ions to effluent is subject to very strict tolerances, given their toxicity.

2. Cationic Fixatives

Cationic dye fixing agents are colourless basic dyes and can react with anionic dye to increase its size; wash fastness is improved but light fastness is adversely affected. Cellulose dyed with any direct dye – irrespective of its structure – can be after-treated in this method. No colour change takes place and reproducibility is excellent with a fear of change in tone – in certain cases. Cationic dye fixing agent splits up into long cation and short anion when direct dye also splits up into long anion and short cation; subsequent reaction forms the complex.

Dye fixing agent : $R_4NCl \leftrightarrow R_4N^+ + Cl^-$

Direct dye : $DSO_3Na \leftrightarrow DSO_3^- + Na^+$

$(R_4N^+ + Cl^-) + (DSO_3^- + Na^+) \rightarrow (DSO_3^- + R_4N^+) + NaCl$

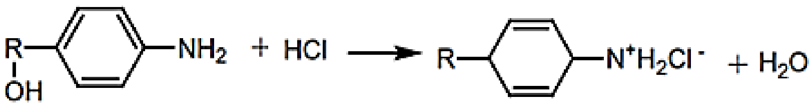
5.13 Renowned Commercial Direct dyes

Brand Name	Manufacturer
Solophenyl	Huntsman (Former Ciba)
Indosol	Archroma (Former Clariant)
Sirius	Dystar (Former Bayer)
Tubantin	CHT Switzerland AG (Former Bezema)

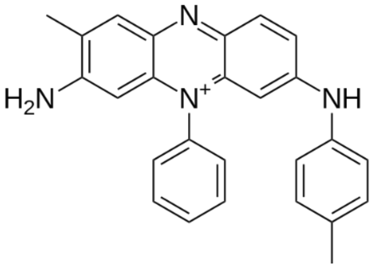
Chapter-6: Basic/Cationic dyes and their application

6.1 What is basic dye/ why are they named so?

The basic dyes are so named because they are derived from organic bases. They retain free or substituted –NH2 groups in their structure, e.g., $-NH_2$, $N(CH_3)_2$, $-N(C_2H_5)$ etc. These dyes are often referred as 'cationic dyes' because they release coloured cation in aqueous solution. Dyes do not show any colour due to absence of chromophore till they are converted to their respective salts, viz. hydrochlorides, oxalates, sulphates, nitrates and zinc chloride double salts etc., which – in turn – are insoluble in water. Basic dyes do not possess systematic nomenclature.



6.2 Which synthetic dye was first discovered?



Mauveine, also known as Aniline Purple and Perkin's mauve, was the first synthetic dye which was discovered serendipitously in 1856 by 18 years old W.H. Perkin. It is also among the first dyes to have been mass-produced.

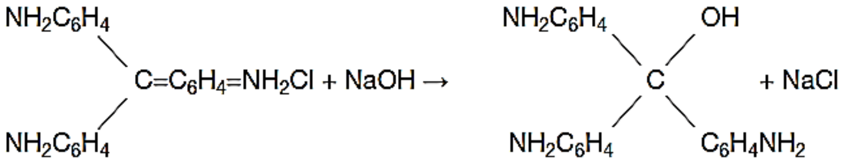
The molecular structure of mauveine proved difficult to determine. Although the research on the molecular structure of mauve began with Perkin himself, it was resolved only in 1994. Further research concluded that it is a mixture of up 12 compounds.

6.3 Properties of Basic dye

1) Basic or cationic dyes have a positive charge on the colour-conferring part of the molecule.
2) Basic dyes are cheaper, soluble in alcohol and methylated spirit but not easily soluble in water.
3) It can be better solubilised in hot water along with little CH_3COOH.
4) Dyes are highly sensitive to alkali and on reaction liberate colourless basic dye.
5) These dyes enable to react with acidic group of fibres like basic dyeable acrylic and cationic dyeable polyester in addition to dyeing of wool, silk and nylon forming ionic linkage.
6) Though basic dyes produce attractive, bright and highly intensive dyes, but their fastness to light and wet on mordanted cotton, protein fibres and acrylic fibres are very low.

6.4 Why is basic dye sensitive to alkali and hard water?

Basic dyes are highly sensitive to alkali and on reaction liberate colourless basic dye.



Use of soft water is a prerequisite in dyeing with basic dye. Presence of calcium or magnesium bicarbonates in water causes precipitation of colourless dye, even presence of metal hydroxides or carbonates cause the same problem. Application of CH_3COOH in bath well before addition of dye reduces both alkalinity and hardness remarkably.

6.5 How can basic dye be applied on cellulosic fibre?

Basic dye possesses no affinity for cellulose and pre-mordanting of the latter is essential to develop affinity for dye. Tannic acid acts as a mordant in dyeing cotton with basic dye using its –OH group to make H-bond with cellulose while –COOH group react with basic dye.

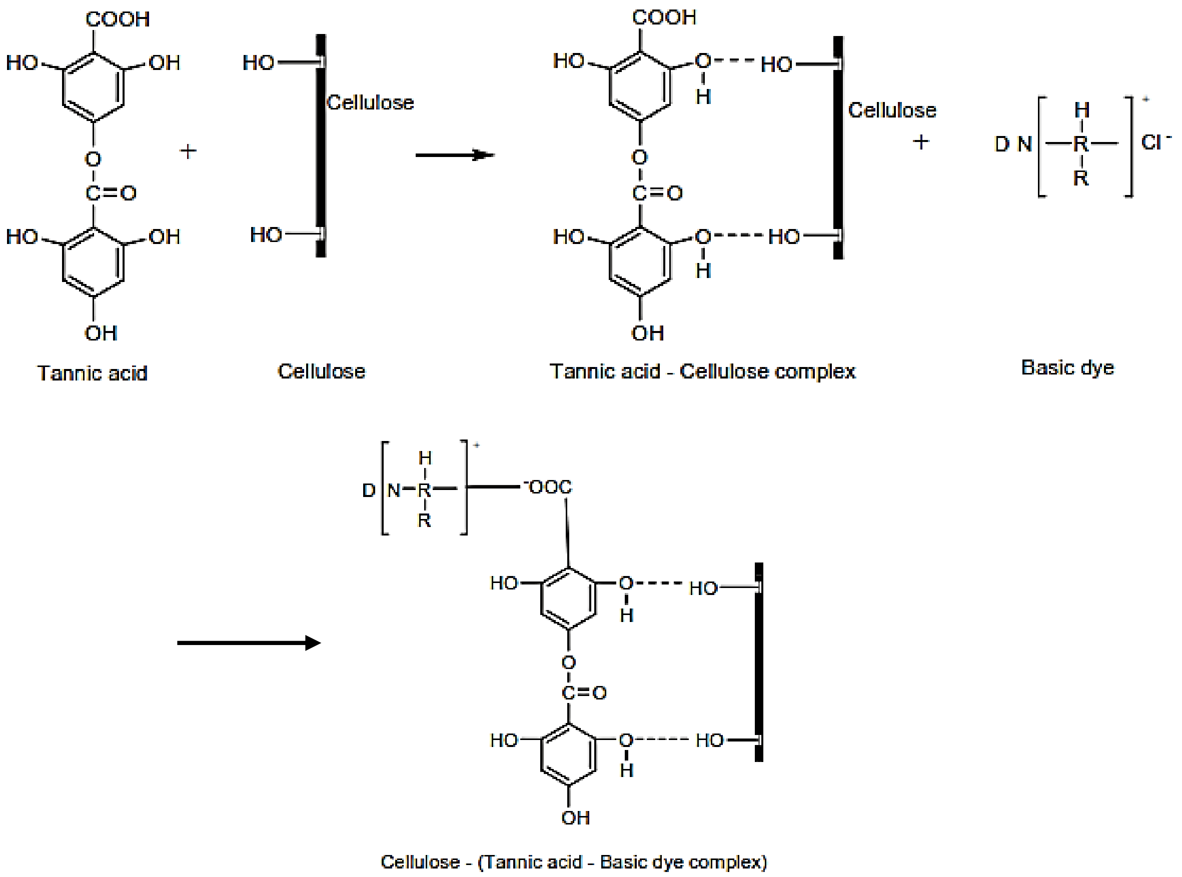


Figure: Sequence of fixation of basic dye on mordanted cellulose

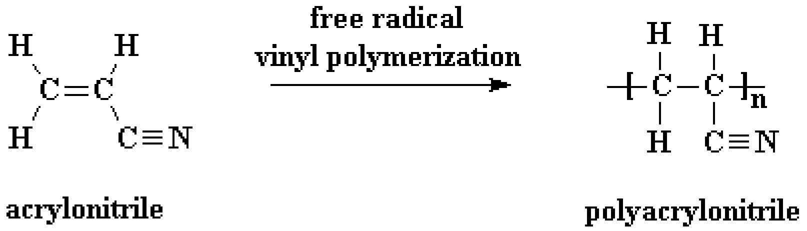
Practical application of basic dye onto cellulose includes three steps, *viz.*

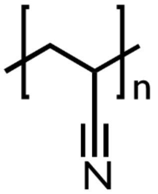
i) Mordanting of cotton with tannic acid,
ii) Fixing with tartar emetic and
iii) Dyeing with basic dye.

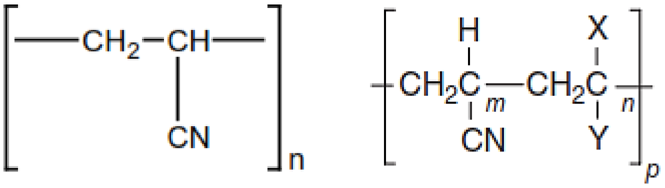
Cotton – mordanted with tannic acid – is treated with tartar emetic –chemically called potassium antimony tartarate $[2\{K(SbO)C_4H_4O_6\}]$ – at cold for 30 min. Tartar emetic is soluble in water and it makes tannic acid insoluble by forming a big molecule of tannic acid–tartar emetic complex, which cannot come out from cotton.

6.6 Why is pure acrylic fibre not dyeable? / How acrylic fibre is made dyeable?

Acrylic fibre is synthesised through polymerisation of acrylonitrile (vinyl cyanide) and has the chemical name polyacrylonitrile (PAN) with the empirical formula where 'n' is the degree of polymerisation. Pure acrylic is brittle, tough and undyeable with any dye due to absence of reactive sites.





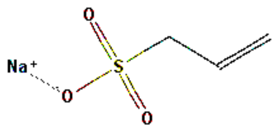
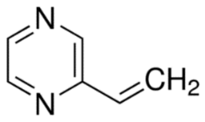
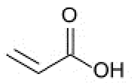
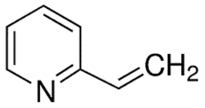


(a) (b)

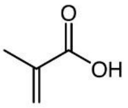
Figure: (a) Pure Acrylic (b) Acrylic with copolymer

To impart textile value, a copolymer of PAN has been produced by adding 5–10% co-monomers. Modern PAN is a copolymer and is produced by adding electrically active ethylenic co-monomers in polymerisation bath. Thus produced PAN has two nomenclatures: if share of co-monomer is ≤15%, it is named acrylic and ≥ 15%, is called modacrylic.

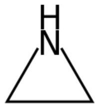
Based on electrical nature of co-monomer, fibre acquires electrical charge, e.g.,

carry negative charge and basic dye is preferred.		carry positive charge and acid dye is preferred.	
Sodium allyl sulphonate		Vinyl pyrazine	
Acrylic acid		Vinyl pyridine	

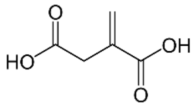
Methacrylic acid



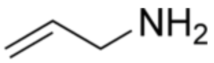
Ethylene imine



Itaconic acid



Allylamine



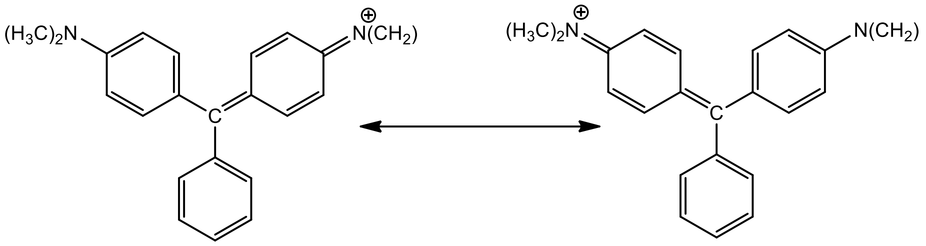
6.7 What are the advantages of dyeing acrylic fibre with basic dye?

Basic dyes are invariably applied on acrylics. It has some advantages over other dyeing methods, *viz.*

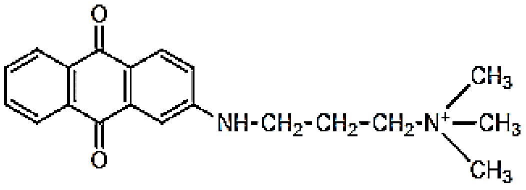
i) All deep shades can be developed with greater ease.
ii) Shades are brighter.
iii) Fastness properties are excellent when special cationic dyes are used. Maximum dye uptake is governed by number of acid groups in fibre though a small amount of dye is also held by dissolution process.

6.8 Various types of basic dyes for acrylic fibre

1. **Group-I dye (conventional basic dye)**
    - The positive charge resonates within the dye structure of dye and remains as part of chromophoric system.
    - These are concentrated basic dye with high tinctorial value and can produce brilliant shades.
    - They are cheaper and light fastness is poor. e.g., Malachite green. The chromophore is TPM, i.e., triphenylmethane.



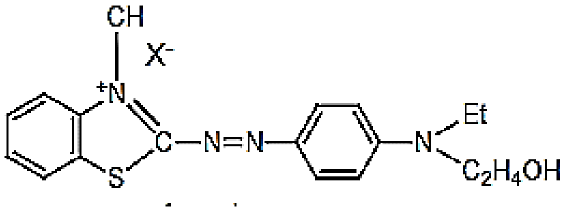
2. **Group-II dye (modified basic dye)**
    - Cost is around ten times higher and less bright than group-I dye.
    - The positive charge is not a part of chromophoric system rather is positioned at some distance from chromophore.



    - Light fastness is around 6. Light fastness is determined by chromophoric system, e.g., anthraquinone, azo etc.

3. **Group-III dye (special cationic dye)**

- These are also called migrating cationic dyes and costs at per with group-II dye.
- Cationic group exists in dye but in balance with halogen to start with, migrate for uniform distribution on PAN and the cationic group is generated during dyeing.
- Halogen (X) is attached to central N and so positive charge of N is in balance with X. At high temperature, X gets detached, N becomes positive and migration becomes excellent.



6.9 Dyeing acrylic fibres with basic dyes

The dyeing mechanism for acrylic fibres could be split into three main steps:

1) Adsorption of the dye molecules at the fibre surface

Acrylic fibres develop a large negative surface charge when immersed in water. However, cationic dyes dissociate forming positive ions leading to the formation of an electrokinetic potential difference between the aqueous dye solution and become adsorbed at surface dye sites

2) Diffusion of the dye from the surface into the fibre

3) Interaction between the dye and fibre.

Once a dye molecule encounters an acid end group, a simple ion-exchange mechanism will take place in which the dye cation displaces H^+, Na^+ or K^+, to form a dye–fibre bond.

6.10 Problems in dyeing acrylic fibres with cationic dyes

- **Problem**

Above the dyeing transition temperature (T_D) under the actual dyeing conditions, cationic dyes tend to exhaust very rapidly over a small range in temperature. Great care is needed at temperatures just above T_D to avoid unlevel dyeing. The rate of diffusion of the cationic dyes into the acrylic fibre is very slow below T_D because of the absence of the required polymer chain mobility. The rate of dyeing increases rapidly above T_D, and can double for every 2.5–3.0 °C increase in temperature.

- **Solution**

The careful temperature control required when dyeing acrylic fibres with cationic dyes is necessary to avoid unlevel dyeings.

The presence of cationic retarder (usually organic ammonium salts) in the dyebath controls the rapid strike and high rate of dyeing of cationic dyes on acrylic fibres. They also compete with the cationic dye for anionic sites in the fibre, thus slowing the rate of adsorption. During dyeing, the cationic auxiliary in the fibre is gradually displaced by the cationic dye.

6.11 Renowned Commercial Basic dye/ Cationic dyestuffs

Brand Name	Manufacturer
Maxilon	Huntsman (Former Ciba)
Doracry	Archroma (Former Clariant)
Astrazon	Dystar (Former Bayer)
Bezacryl	CHT Switzerland AG (Former Bezema)

Chapter-7: Vat dyes and their application

7.1 What is vat dye? / Why are they so named?

A vat dye is defined as a water-insoluble dye, usually containing keto groups, which is normally applied to the fibre from an alkaline aqueous solution of the reduced enol (leuco) form, which is subsequently oxidised in the fibre to the insoluble form. In ancient times, dyeing was often carried out in wooden vat assigning the name 'vat dye'.

7.2 Basic principle of vat dyeing

The overall process of vat dyeing involves three key steps:

1) Reduction of the pigment to the soluble leuco compound, a process called vatting;
2) Absorption of the leuco compound by the cotton during dyeing;
3) Oxidation of the absorbed leuco compound in the cotton, reforming the insoluble pigment inside the fibres.

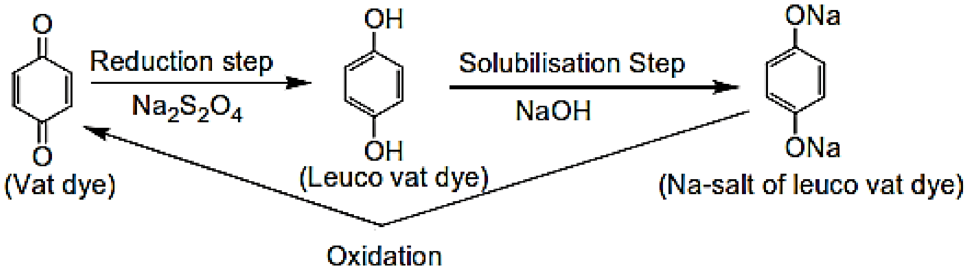


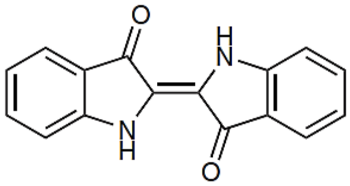
Figure: Basic principle of dyeing cotton with vat dye

The use of strongly alkaline solutions (pH 12–14) for vatting and dyeing limits the use of most vat dyes to cellulosic fibres.

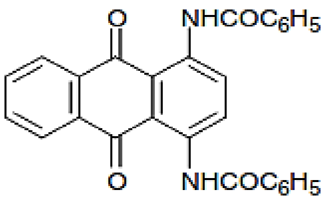
7.3 Classification of vat dye on the basis of Chemical Constitution

As per chemical constitution, vat dyes can be classified into following two classes:

1. Indigoid (e.g. CI Vat Blue 1)
2. Anthraquinonoid (CI Vat Red 42)



CI Vat Blue 1



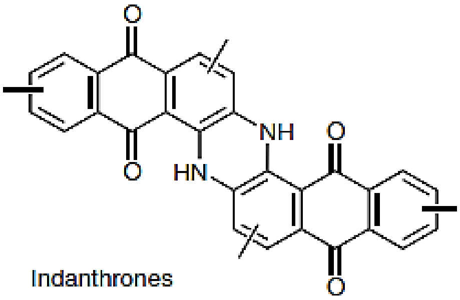
CI Vat Red 42

Indigoid dyes have limited range of colors. These form of dyes can dye nylon, wool and cotton. Most of the vat dyes belong to anthraquinone groups because indogoid have lost their practical importance. All the browns, khakis, olives, grey products belong to this class.

7.4 Classification of vat dye on the basis of application

Vat dyes are classified into four groups according to method of application, depending on the solubility, ease of vatting, optimum conditions of dyeing etc.

1. IK Class (K for cold or kalt in German)
2. IW Class (W for warm)
3. IN Class (N for normal)
4. IN Spl Class (Spl for special dyes)


Indanthrones

Dye class	Vatting temp (°C)	Dyeing temp (°C)	$Na_2S_2O_4$	NaOH	Electrolyte
IK	35–50	30	Less	Less	Higher
IW	45–50	40–45	Moderate	Moderate	Moderate
IN	55–60	50–55	Higher	Higher	Less
IN special	≥60	≥ 60	Very high	Very high	Not required

7.5 Application of vat dye on cellulose

Typical recipe

Vatting and Dyeing:

- Dye – 1%
- T R oil – a little
- $Na_2S_2O_4$ – ‘A’ g/l (As per Table)
- NaOH – ‘B’ g/l (As per Table)
- Salt – ‘C’ g/l (As per Table)
- Vatting temperature – x° C (As per Table)
- Dyeing temperature – (x–5)°C (As per Table)

Oxidation:

- H_2O_2 (35%) – 1–2 ml/l at 50–60°C for 15–20 min

Soaping:

- Na_2CO_3 and soap (0.5 g/l each) at boil for 15–30 min or steaming only.

7.6 Properties of Vat dye

i) **Solubility:** Vat dyes are insoluble in water and nonionic in nature;

ii) **Application:** These are used predominantly for dyeing cellulosic fibres. Although the leuco dyes also have substantivity for wool and nylon, technical reasons restrict their commercial significance for these fibres to the dyeing of nylon/cotton blends.

iii) **Application Mechanism:** These are converted to leuco compounds on reduction followed by solubilisation with alkali in that state these show substantivity towards cellulose. After dyeing, parent dye structure is recovered by oxidising it within fibre.

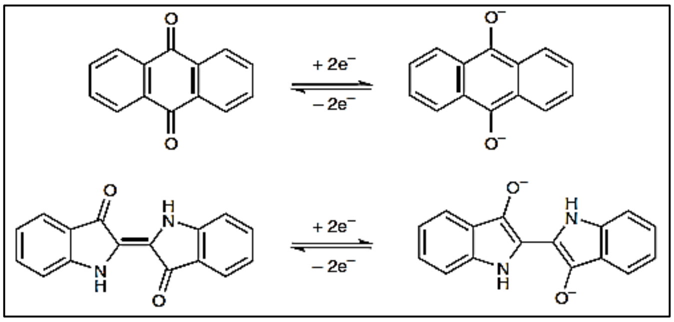
iv) **Colour Fastness:** Dyeings produced with vat dyes on cellulosic fibres have an overall standard of fastness higher than is achieved with other classes of dyes.

v) **Shade Range:** Dyes are costlier, full shade range is available with high tinctorial power.

7.7 What is Reduction-Oxidation (Redox) Potential or ORP? / Why is it important in vat dyeing?

The ***redox potential*** is a measure of the tendency of a chemical species to be reduced and thereby acquire electrons. A given compound will possess a particular redox potential: the more negative the potential, the greater the tendency of that compound to be reduced (i.e. to acquire electrons). In aqueous solution, the resulting change in the charge of the system can be quantified by measuring the voltage **(in mV)** between a standard **electrode.**

Thus, **reducing agents** have **negative redox** potentials whereas **oxidising agents** have **positive redox** potentials.



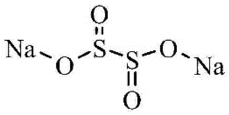
In the reduction of vat dyes, the reduced derivative is in equilibrium with the oxidised derivative and, therefore, this reversible process constitutes a *reduction/oxidation system* or *redox system.* Vat dyes generally display redox potentials in aqueous media in the range of **-770 to -1000 mV,** the majority being in the region **-900 to -950 mV**, while that of indigo is **600-850 mV.**

Any successful reducing agent should possess a redox potential lower than that of the compound to be reduced. Thus, powerful reducing agents are commonly utilised in vat dyeing amongst which **sodium dithionite** (aka **sodium hydrosulfite; $Na_2S_2O_4$;** redox potential **-970 mV**) is of major importance.

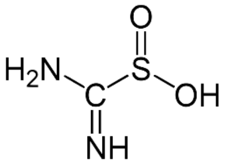
7.8 Reducing agents for vat dyeing

1. Sodium Dithionite (Redox Potential –970 mV)

The most important reducing agent in vat dyeing is sodium dithionite, generally referred to as hydrosulphite or hydros. It has a reduction potential that is sufficiently negative for all practical requirements.



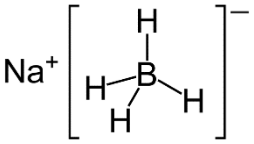
$Na_2S_2O_4$



2. Thiourea Dioxide (Redox Potential -1100 mV)

It has a stronger reducing effect than hydrosulfite. Therefore, with sensitive dyes, a risk of over-reduction exists.

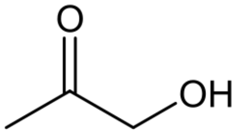
3. Sodium borohydride (Redox Potential -700 mV)



$NaBH_4$

It reacts too slowly for vat dyeing.

4. Hydroxyacetone (redox potential -810 mV)



The reducing effect of hydroxyacetone is much weaker so it cannot replace hydrosulfite in all applications.

7.9 Problem of over-reduction of vat dyes

When $Na_2S_2O_4$ is applied in too-excess or when temperature of vatting is not maintained properly, few vat dyes get over-reduced and pose problem in developing true shade. Only two >C=O groups of indanthrene blue dyes should be reduced under ideal conditions of reaction, but when over-reduction occurs, all four >C=O groups are reduced.

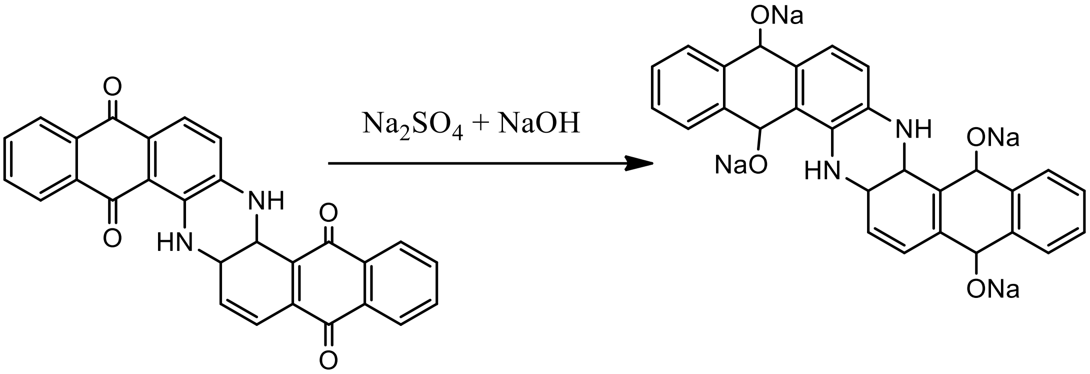


Figure: Sample over reduction of vat dye.

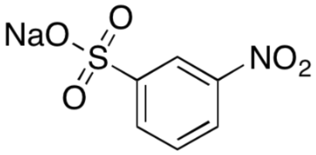
7.10 Oxidation agent after vat dyeing

When the exhaustion process is complete, the dyeing is rinsed to remove loose dye and most of the residual reducing agent and alkali. The leuco dye is then reconverted into its original form by oxidation. This is generally carried out with

i) Hydrogen peroxide (H_2O_2)

ii) Sodium perborate ($NaBO_3$)

iii) Sodium *m*-nitrobenzenesulphonate e.g. Ludigol (BASF).



7.11 What is solubilized vat dye?

Reduction of vat dye and subsequent stabilisation of reduced bath is a cumbersome work; lack of control over it produces unlevel dyeing. Reduced and stabilized vat dye is called solubilised vat dye – chemically it is a 'sodium salt of sulphuric ester of leuco vat dye' which requires neither reduction nor solubilisation during application. Affinity of this dye class is too less than that of parent vat dye for cotton. The vat dyestuff from which solubilised vat dye is prepared, is reduced by its manufacturer, stabilised and supplied in powder or paste form to the dyer. Solubilised vat dyes are popularly known as indigosol dyes as BASF (Germany) was the first to introduce these in the market with the brand name – indigosol.

7.12 Methods of manufacturing solubilized vat dye

There are two methods of manufacturing this dye:

1) **Chloro-sulphonic acid method** in which vat dye is reduced with Na at required temperature in the presence of pyridine. The reduced dye is treated with chloro-sulphonic acid followed by with sodium hydroxide.

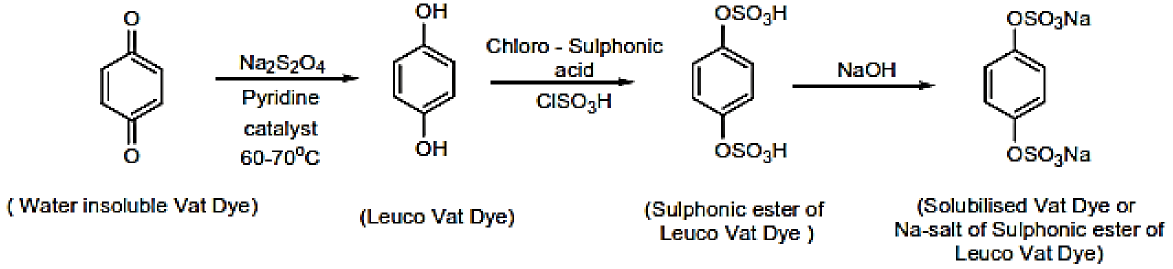


Figure: Manufacture of solubilised vat dye in chlorosulphonic acid method

2) **In second method,** parent vat dye is treated with copper–pyridine complex and finally converted into sodium salt of leuco sulphate ester.

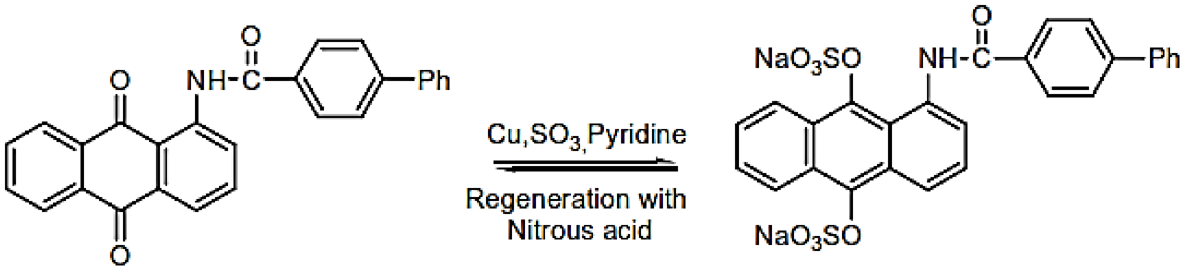


Figure: Manufacture of solubilised vat dye in copper–pyridine complex method

After dyeing, original vat dye structure is restored using an acidic oxidising agent, e.g., nitrous acid. The Na-salt of sulphuric ester of vat dye is mixed with a stabiliser – like urea. After dyeing, H_2SO_4 along with $NaNO_2$ or K_2Cr_2O7 is applied to oxidise solubilised vat dye at 50–70°C when the dye is hydrolysed and oxidised back to parent vat dye.

7.13 Application of solubilized vat dye

Dyeing of cotton with these dyes follows a two-stage method:

i) Dyeing is carried out in an alkaline or neutral bath (for cellulose) or acidic dye bath (for protein fibres); exhaustion is controlled by manipulating temperature and salt.

ii) Regeneration of dye is carried out through oxidation of dyeings with HNO_2 – the latter is produced in bath by applying $NaNO_2$ and H_2SO_4.

Each dye has its own condition of time, temperature, concentration of H_2SO_4 and $NaNO_2$.

Typical recipe

Dye - x%
Na_2CO_3 - 2 g/l
$NaNO_2$ - 3–4 g/l
NaCl - 50 g/l
H_2SO_4 (70%) - 5–10 g/l

Functions of chemicals

- **Alkali**

Dyes either in powder state or solution form ensures better stability in alkaline pH. If alkali is not added, dye is hydrolysed and premature oxidation occurs in bath itself.

- **$NaNO_2$**

It works in two ways:

(a) it produces HNO_2, the oxidising agent for dye through reaction with H_2SO_4

(b) being an electrolyte, it promotes exhaustion of dye.

$$H_2SO_4 + 2NaNO_2 \rightarrow 2HNO_2 + Na_2SO_4$$

- **NaCl**

Exhausting agent concentration depends on affinity of dye – higher the affinity lesser the concentration (10–50 g/l).

7.14 Properties of solubilized vat dye

- **Solubility**: Dyes are mostly soluble in hot water and a few are soluble in presence of little soda ash; solubility can be improved by adding urea at 50–60°C.
- **Shade:** Shades are brilliant and fastness is equivalent to those with corresponding vat dyes. Range of shades is limited to blue, orange, purple, pink, yellow, green and golden – all in light shades.
- **Affinity:** Due to negligible affinity for cellulose, soda ash is added to enhance dye uptake. Dyes possess excellent affinity for protein fibres; the affinity is further enhanced on addition of mild acid, e.g., HCOOH, CHCOOH in bath.
- **Application:** The main use of this dye is in dyeing pale shades on cotton and polyester/cotton blend with excellent colour fastness.
- **Other:** Dyes are costly but levelling property is excellent.

7.15 Why indigo dye is still widely used to produce faded jeans?

Although indigo is a member of vat dye class, in reduced and solubilised state, indigo possesses little affinity for cotton the extent of affinity is too less to exercise exhaust dyeing; rather multi dip/nip padding technique with intermediate air oxidation is followed for gradual build-up of shade. Denim is exclusively dyed with indigo to produce brilliant blue shades with desired wash-down effect.

Indigo dye gives more intensive surface dyeing which is called 'ring dyeing' – where only a few surface layers are dyed leaving interior of yarn undyed due to the absence of adequate time for penetration and thorough distribution. Efficient wash-down property of indigo dyed yarn depends on the amount of dye present on yarn surface. It is the 10.5–11.5 pH range which gives ring dyeing with desired washing performance, poor diffusion of dye inside and a deeper shade with lesser amount of indigo. Dyeing at higher pH ranges offers relatively lighter shades due to thorough diffusion as well as distribution of indigo with the consequence of lower wash-down property.

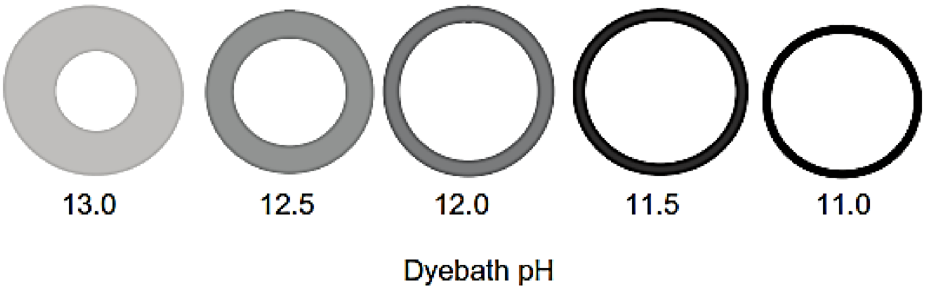


Figure: Distribution of indigo in the cross-section of cotton denim yarn at different pH

7.16 Renowned Commercial vat dye

Brand Name	Manufacturer
Novasol	Huntsman (Former Ciba)
Indanthren	Dystar (Former BASF)
Bezathren	CHT Switzerland AG (Former Bezema)

Chapter-8: Introduction to Textile Printing

8.1 What is printing?

Printing involves localised coloration. This localised application of colour must be carried out with precision since each colour of the image is applied via a screen. This is usually achieved by applying thickened pastes containing dyes or pigments onto a fabric surface according to a given colour design.

8.2 Flow chart of Printing

Preparation of the fabric
↓
Preparation of the printing paste
↓
Making an impression of the paste on the fabric
↓
Drying of the printed fabric
↓
Steaming of the printed fabric
↓
After treatment

8.3 Print Paste Formulation

The print paste is the medium by which the colorant (dye or pigment) is applied to the textile substrate. In general, the formulation depends upon a number of factors, including the dye or pigments being printed, the substrate and the fastness requirements of the print.

The ingredients of the print paste and their functions are listed as follows:

- **Colorant –** Dye
- **Thickener –** To provide print paste viscosity.
- **Humectant/Hygroscopic Agent –** To maintain moisture content during printing and fixation (steaming). Most commonly used is urea.
- **Acid/Alkali –** Depends upon dye class being used.
- **Oxidising agent –** Prevents 'frosting' of prints or reduction of dye during steaming. Compounds such as sodium *m*-nitrobenzene sulphonate.
- **Water –** Solvent for the ingredients.

8.4 Thickeners

Print paste thickeners are colourless materials that form viscous pastes with water. The function of the thickener is to ensure that the print paste has satisfactory *viscoelastic* properties. The term 'viscoelastic' relates to viscosity and how viscosity changes during the application of the print paste to the fabric.

8.5 Classification of thickener

Thickeners may be divided chemically into three main types depending upon their chemical constitution: natural products, modified natural products and synthetic products.

1. Natural Products

Natural products are sugar-based carbohydrates and are categorised as polysaccharides. They are obtained from various natural sources:

- Starch-based products, which include British gums, guar and locust bean gum obtained from plant seeds
- Alginates, obtained from seaweed
- Xanthans obtained from microorganisms
- Cellulose ethers, obtained from cellulose pulps

2. Modified Natural Products

- Carboxymethyl cellulose (CMC)

3. Synthetic Products

- Emulsions

8.6 The requirements of a thickener

It may vary depending upon the dye class being printed and the substrate. However the thickener should have the following properties:

i) Compatibility with all the other components of the print paste.
ii) Easy to dissolve in water.
iii) Stable during the printing and fixation stages.
iv) Capable of being removed in the final print washing stage.

8.7 Stages of Printing

The printing process can be broken down into three stages:

1) Transport
2) Fixation
3) Wash-off

Each stage is unique to the substrate being printed, the dye application class or pigment being used and the type of design being printed.

1) Transport

This may be either the dye being forced through the mesh of a flat or rotary screen or deposited from the cell of a copper roller. The dye is transported to the fabric surface, and upon drying the paste forms a thin film containing the dye.

2) Fixation

Fixation is the movement of the dye from the film to the interior of the substrate by diffusion. The dried print is subjected to steam to facilitate the diffusion of the dye into the substrate.

The type of steam used during the fixation process is important since this can influence the duration of the fixation process. Steaming may be conducted by using:

- ***Saturated steam-*** Saturated steam is steam that contains droplets of water and the temperature is typically 104 °C.
- ***Dry saturated steam-*** Dry saturated steam is steam that does not contain droplets of liquid water.
- ***Superheated steam-*** Superheated steam is dry saturated steam that has been heated to a higher temperature (between 130 and 160 °C) for the pressure involved.

Regardless of the type of steam employed for the fixation process, the steam must provide sufficient 'water' to swell the thickener film so that movement (diffusion) of the dye is possible.

The time and conditions for fixation in steam vary with the properties of the dyes and fibres used, ranging from **10 s to 60 min** in steam at **200 to 100°C.** Technical and economic factors have encouraged the use of higher temperatures and shorter times, and the change from batchwise to continuous processes.

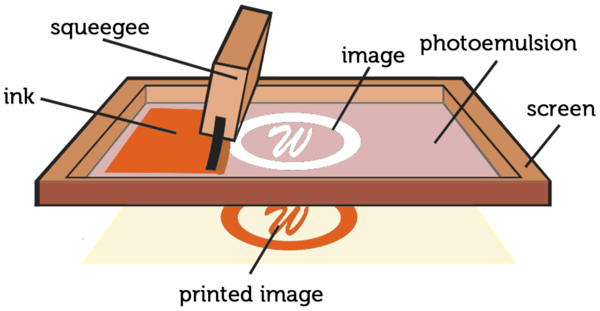
3) Wash-off

Following steaming it is essential to wash off the printed steamed fabric in order to remove thickener, ancillary chemicals and unfixed dye. The wash-off provides the printed textile substrate with the full wet fastness performance of the print.

8.8 Methods of Printing

Printing methods in terms of the machinery used to deliver the print paste and the mode by which paste is delivered to the substrate, be it

- Flat screen printing
- Rotary screen printing
- Copper roller printing
- Ink jet printing etc.

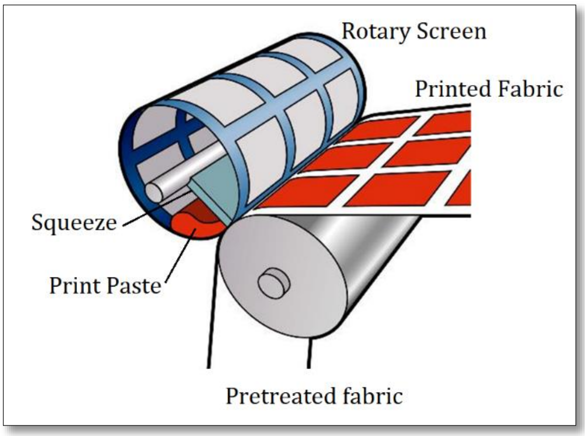


1. Flat Screen Printing

- As the name suggests, the screens for this printing method are flat as opposed to circular as in rotary screen printing.
- The screen is a woven mesh, made from either polyester or polyamide.
- The mesh is stretched over a rectangular frame, originally made from wood, but now made from metal alloy to reduce weight and increase durability.
- During printing, the screen usually lies across the fabric width.
- The polyester fabric only allows the printing paste to pass through the mesh in those areas corresponding to the design being printed.
- A suitable coating blocks the remaining areas.
- There is a screen for printing each colour and each successive screen sits on the fabric in the exact position for accurate registration of the multicolour design.
- Machines of this printing may be manual, semi-automatic and fully automatic.

2. Rotary screen printing

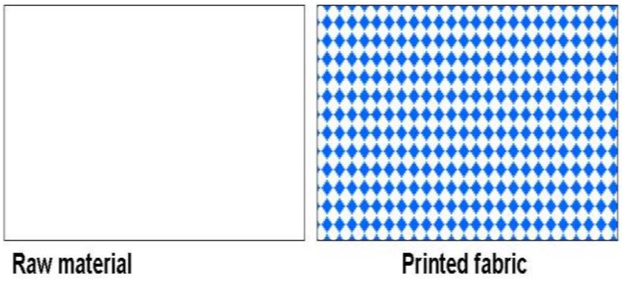
- In rotary screen printing, coloured paste is forced through the open areas of a cylindrical printing screen that rotates as the fabric moves beneath it.
- In contrast to intermittent flat screen printing, rotary screen printing is fully continuous with fabric speeds up to 50 m min^{-1}, if adequate drying capacity is available.
- Rotary screen printing is now by far the major printing method for textile fabrics.



8.9 Styles of printing

A colored design on a white or a differently colored background can be produced on fabrics by using different styles of printing such as –

1. Direct style
2. Discharge style
3. Resist style
4. Flock style
5. Burn out style

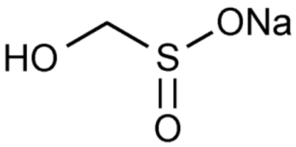


1. Direct style Printing

- ➢ Direct printing is probably the simplest printing technique, in which colour is applied directly onto the fabric, followed by fixation.
- ➢ This style of printing produces a coloured print on a white background with each colour of the design requiring a separate screen. All the dyes are suitable in this style.

2. Discharge style

- ➢ In discharge printing, the background colour of the print is firstly applied to the fabric prior to printing. This background colour can be applied by exhaust batch dyeing or by continuous dyeing processes.
- ➢ A print paste that, instead of containing dye, contains a reducing agent is then applied to the local areas of the fabric required by the design.
- ➢ It is essential to the printing style that the background colour is produced from dyestuffs that can be 'discharged', that is, destroyed by chemical reduction in order for the pattern to be displayed after printing of the discharge paste.

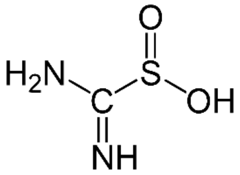


Common discharging chemicals are based on:

i) Formaldehyde sulphoxylates such as sodium formaldehyde sulphoxylate (C.I. Reducing Agent 2).

ii) Thiourea dioxide (C.I. Reducing Agent 11)

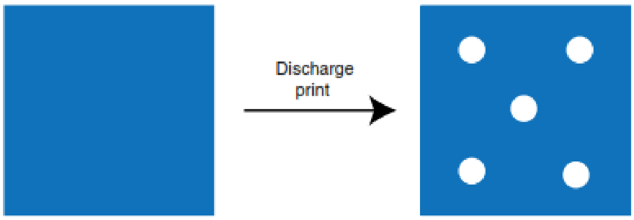
Rongalite, also called Rongalit (registered trademark of BASF)



There are two types of discharge printing.

i) White Discharge Print

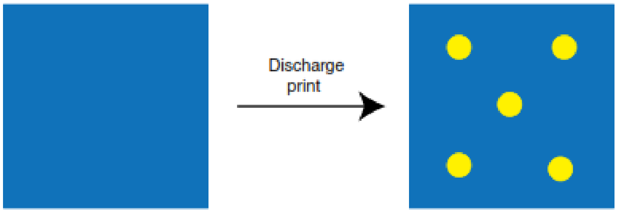
- Here, the chemical reduction leaves a white image on the coloured background.



White discharge

ii) Colour Discharge/ illuminated discharge Printing

- It is possible to create an 'illuminated discharge' by incorporating a dye into the discharging paste.
- The dye or pigment in the paste must be resistant to the discharge chemical present also, so that it remains on the fabric when the illuminated discharge paste is printed.



Illuminated discharge

- The illuminated discharge paste destroys the background colour of the print, but the 'illuminating' colour remains.

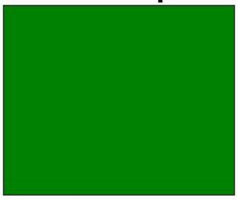
3. **Resist Printing**

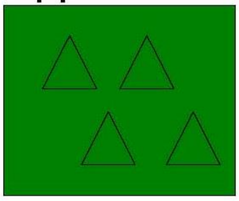
- Resist printing, also known as reserve printing, involves printing the white fabric first with a paste known as a *resist paste*.
- The resist paste prevents the dye from being taken up in a subsequent dyeing process.
- The final result resembles much the same as that achieved using the discharge printing route. However, the resist printing route allows the use of a wider range of dyes.

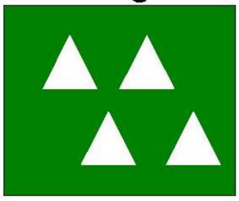
There are two types of resist printing technique depending upon how the resist is achieved:

i) Mechanical resist, which is achieved by using materials such as resin, clay or wax. These form a physical barrier between the fabric and the dye and are used mainly for coarse decorative styles.

ii) Chemical resist printing, where the fabric is printed with the resist paste followed by overdyeing, either by batch or continuous methods. The resist paste prevents fixation or development of the ground colour by chemically reacting either with the dye or with the reagents necessary for the fixation of the dye.


Raw material


Printed fabric


Washed fabric

8.10 Typical Printing Recipe with direct dye on cotton fabric

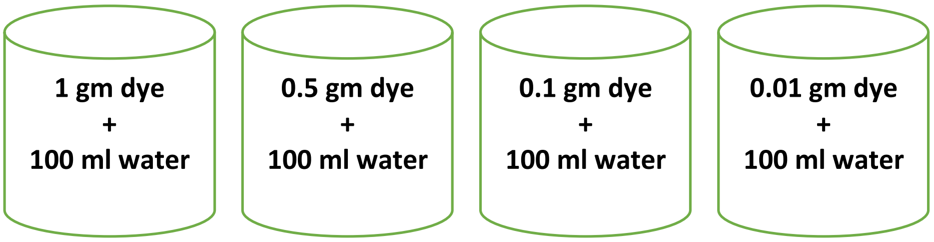
Chemicals/ Parameters	Quantity (g)
Direct Dyes	20
Dispersing Agent (TRO)	10
Thickener (Natural Gum), 10% Stock Paste	500
Hygroscopic Agent (Glycerin)	50
Alkali (TSP)	20
Water	Rest to make 1 kg paste

8.11 Typical Printing Recipe with acid dye on silk fabric

Chemicals/Parameters	Quantity (g)
Acid Dyes	30
Thickener (Natural Gum), 10% Stock Paste	500
Hygroscopic Agent (Glycerin)	50
Acetic Acid (40%)	50
Tartaric Acid (40%)	50
Water	Rest to make 1 kg paste

Chapter-9: Calculation in Laboratory Dyeing

9.1 Stock Solution or Dispersion



1% stock dye solution

0.5 % stock dye solution

0.1% stock dye solution

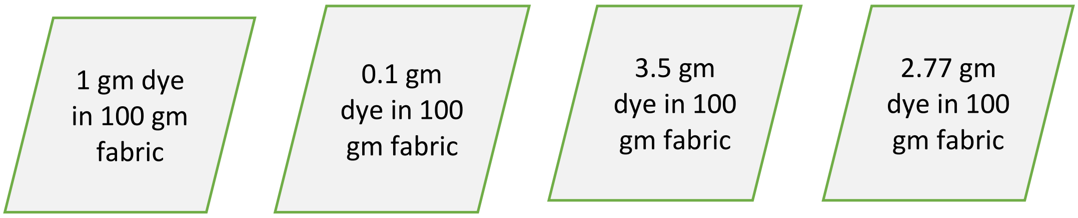
0.01% stock dye solution

For a 0.4% stock solution or dispersion, 100 ml is normally prepared, i.e. 0.4 g in 100 ml or 2.0 g in 500 ml.

Questions:

1. Calculate the stock% of 2 gm/L dye solution.
2. Calculate the dye concentration in mg/L of a 0.06% stock solution.
3. How much dye will require to prepare 450 ml dye solution of 0.2% stock?

9.2 Shade%



1% Shade

0.1% Shade

3.5% Shade

2.77% Shade

Questions:

1. How much dye will be required to dye 2.8 kg fabric with 1.65% shade?
2. If 3.4 kg dye is applied to dye 250 kg knitted fabric, calculate the shade%.
3. If 1.5 tons fabric is dyed with combined shade namely Red dye= 1.8%, Yellow dye = 1.1% and Blue dye= 0.4%, calculate the consumption of these three dyes.

9.3 Calculation of required dye solution in laboratory dyeing

Mass of the sample = 4 gm

Shade% = 2%

Stock Solution% = 0.4%

$$\text{Required dye solution (ml)} = \frac{\text{\% depth x weight of specimen}}{\text{\% of stock or dispersion}}$$

$$= \frac{2.0 \times 4.0}{0.4}$$

= 20.0 ml

Questions

1. In the above case, if the lab technician prepare 0.38% stock mistakenly, what will be the actual shade% applied?

   Answer:

$$\text{20.0 ml pipetted out} = \frac{\text{x\%} \times 4.0}{0.38}$$

$$= \text{\% applied} = \mathbf{1.9}\%$$

2. In the above case, if the lab technician prepare 0.42% stock mistakenly, what will be the actual shade% applied?

   Answer:

$$\text{20.0 ml pipetted out} = \frac{\text{x\%} \times 4.0}{0.42}$$

= % applied = **2.1%**

3. In the above case, if the lab technician prepare a stock solution by adding 2.2 gm dye in 500 ml water what will be the actual shade% applied?

9.4 Dyebath concentration & Exhaustion%

$$\text{\% Exhaustion (\%E)} = \frac{\text{Amount of dye in fibre at end of dyeing}}{\text{Amount of dye in dyebath at start of dyeing}} \text{ x 100 \%}$$

$$\%\text{E} = \frac{C_0 - C_t}{C_0} \times 100\%$$

C_0 = Initial Concentration of dyebath.

C_t = Concentration of dyebath at the end of dyeing.

Questions

Fabric mass = 5 gm

M:L = 1:25

Shade% = 1.65%

1. Calculate the initial dyebath concentration in g/L and mg/L.
2. If the residual dyebath concentration is 110 mg/L, Calculate the Exhaustion% of dye in this case.
3. How much dye will remain in fibre at the end of this dyeing?
4. Calculate the amount of dye that will present in the effluent if 550 kg knitted fabric is dyed at 1:8 material liquor ratio. [Consider the same exhaustion% in laboratory and bulk dyeing]

9.5 Exhaustion versus Time profile

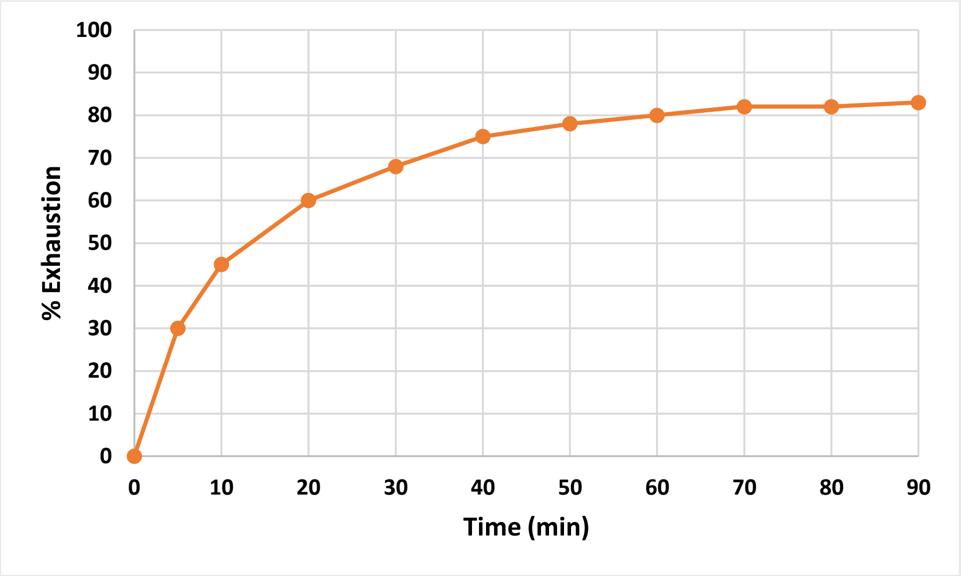


Figure: An exhaustion% profile of cotton fibre dyeing with direct dye.

Questions:

1. Find out the exhaustion% after 30 minutes and 1 hour.
2. Find out the time required for 50% dye exhaustion.
3. Calculate the amount of dye that will present in the fibre after 45 minutes dyeing of 550 kg knitted fabric at 2.2% shade.
4. Calculate the amount of dye that will present in effluent after 60 minutes dyeing of 550 kg knitted fabric at 1.9% shade.
5. Calculate the initial concentration of dyebath if 1100 Kg fabric is dyed at 1:6 Material to liquor ratio with 3.25% shade.
6. Calculate the concentration of dyebath after 50 minutes dyeing of 1100 Kg fabric at 1:6 Material to liquor ratio and 3.25% shade using the above mentioned exhaustion profile.