KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS

DEPARTMENT OF CHEMISTRY

	MAJOR ELECTIVE-II	**Semester -VI**
15CHU603B	**DYE CHEMISTRY**	**5H- 5C**

Instruction Hours/week:L: 5 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Scope

This course centered on dyeing and its application to other sectors. The course allows one to get a fundamental idea about the dye Chemistry. The course helps the students in improving their diverse skills in various areas such as laboratory skills, numerical and computing skills, ability to approach to the problems both analytically and logically, time management skills, etc. The principles in this course are used in almost every field such as medicines, food products, and electronics industry.

Objectives

1. To introduce the application of colourants (dyes) on various substrate- fibres, food, plastics, etc.
2. To provide students with opportunities to appreciate and know the basic skills in dyeing.
3. To learn about different types of dyes like Direct, Acid & basic dyes, Mordant, Azo and Vat Dyes, Disperse dyes and about optical brightening agents.

UNIT I

Colour and chemical constitution Colour and chemical constitution - chromophore, auxochrome and resonance, various theories; History of natural and synthetic dyes; Names of commercial dyes; Study of raw materials and dyestuff intermediates; Unit operations - nitration, sulphonation, halogenation, amination, diazotisation and alkali fusion; Classification of dyes based on chemical constitution.

UNIT II

Direct, Acid and Basic Dyes

Direct cotton dyes (substantive dyes) – Classification, properties, structure and mechanism of dyeing, post treatment of dyeing.

Acid dyes and Basic dyes – Classification, Characteristics, Mechanism of dyeing, Nature of affinity on cellulose and protein fibres.

UNIT III

Mordant, Azo and Vat Dyes

Mordant dyes – classification, methods of application; Metal complex dyes – types of bond formation between dye and various fibres.

Azo dyes – Azoic coupling components, protective colloids, electrolytes, stabilisation of diazonium salts, principles and application.

Vat dyes and solubilised vat dyes – classification, methods of application, principles and application, Stripping agents and correction of faulty dyeing.

UNIT IV

Disperse dyes

Chemistry involved in the production of Aniline black; Prussian black and phthalocyanines.

Disperse dyes - classification based on chemical structure, properties and principles of application; Solvent soluble dyes - Nigrosines and Indulines; Cyanine dyes.

UNIT V

Colour and Brightening Agents

Fluorescent brightening agents (FBA) - Theory and applications; Identification and estimation of dyes on fibres; The action of light on dyes and dyed fibres; Mechanism of fading.

TEXT BOOKS:

1. K. Venkataraman, The chemistry of synthetic dyes Part I & II, Academic Press, New York, 1952.
2. V. A. Shenai, Introduction to Chemistry of Dyesuffs, Sevak Prakashan Pub., Mumbai, 1991.

REFERENCES:

1. V. A. Shenai, Chemistry of Dyes and Principles of Dyeing Vol.-II, Sevak Prakashan, Mumbai, 1987.
2. V. A. Shenai, Ecology and Textiles, Sevak Publications, Mumbai, 1997.
3. D. M. Nunn, The Dyeing of Synthetic Polymer and Acetate Fibres, Dyers Company, Publication Trust, 1979.
4. V. A. Shenai, Toxicity of Dyes and Intermediates, Sevak Publications, Mumbai, 1998.
5. Directory of safe dyes conforming to German Consumer Goods Ordinances, The Dyestuff Manufacturers Association of India, 1996.

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LECTURE PLAN
DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. J. BALAJI & Mr. M. DINESH KUMAR
SUBJECT NAME: Major Elective II (Dye chemistry) SUB.CODE:15CHU603B
SEMESTER: VI CLASS: III B.Sc Chemistry

S.No	Lecture duration period	Topics to be covered	Support material/ Page No.
		UNIT I	
1.	1	Colour and chemical composition	T1:78-79
2.	1	Chromophore, Auxochrome and resonance various theories	T1: 80-87
3.	1	History of natural and synthetic dyes	T1: 1-9
4.	1	Name of commercial dyes	T1: 22
5.	1	Study of raw materials and dyestuff intermediates	T1: 10-11
6.	1	Unit operations	T1: 10-11
7.	1	Nitration	T1: 11-17
8.	1	Sulphonation	T1: 18-32
9.	1	Halogenation	T1: 34-40
10.	1	Amination	T1: 40-43
11.	1	Diazotization	T1: 46
12.	1	Alkali fusion	T1: 47
13.	2	Classification of dyes based on chemical composition	T1: 71-77
14.	1	Revision and discussion of important questions	
	Total No of Hours Planned For Unit I = 15		

		UNIT II	
1.	1	Direct cotton dyes (Substantive dyes)	T1: 67
2.	2	Classification, properties of dyes	T1: 66, T2: 40-42
3.	2	Structure & mechanism of dyeing	T2: 216-221
4.	1	Post treatment of dyeing	T2: 220-221
5.	2	Classification of acids & basic dyes	T1: 66-67
6.	1	Characteristics of acids & basic dyes	T1: 66-67
7.	1	Mechanism of dyeing	T2: 218-220
8.	1	Nature of affinity on cellulose	T2: 278-280
9.	1	Nature of affinity on protein fibre	T2: 276-278
10.	1	Revision and discussion of important questions	
	Total No of Hours Planned For Unit II = 13		
		UNIT III	
1.	1	Mordant, azo and vat dyes	T1: 67
2.	1	Classification of mordant dyes	T1: 67-68
3.	1	Application methods of mordant dyes	T1: 68
4.	1	Metal complex dyes	T1: 136-153
5.	2	Types of bond formation between dye and various fibres	T2: 178-179
6.	1	Azoic coupling compounds	T2: 233-236
7.	1	Protective colloids	T2: 170-171
8.	1	Electrolytes	T2: 169-171
9.	1	Stabilization of diazonium salts	T2: 49-52
10.	1	Principle & application of azo dyes	T1: 106-135
11.	1	Principle & application of vat dyes	T1: 286-291
12.	1	Classification of vat dyes	T1: 290-291
13.	1	Stripping agents	T2: 252-254
14.	1	Correction of faulty dyeing	T2: 224-226
15.	1	Revision and discussion of important questions	
	Total No of Hours Planned For Unit III = 16		
		UNIT IV	

1.	1	Disperse dyes	T2: 179-180
2.	1	Chemistry involved in Aniline black	T2: 429
3.	1	Prussian black	T2: 430
4.	1	Phthalocyanines	T1: 276-285
5.	2	Disperse dyes - Classification	T2: 236-243
6.	1	Properties	T2: 238-240
7.	1	Principles of application	T2: 240-243
8.	2	Solvent soluble dyes	T1: 302, T2: 133
9.	1	Nigrosines	T1: 298
10.	1	indulines	T2: 102
11.	1	Cyanine dyes	T1: 54-59
12.	1	Revision and discussion of important questions	
	Total No of Hours Planned For Unit IV = 14		
		UNIT V	
1.	1	Colour and brightening agents	T1: 292
2.	1	Fluorescent brightening agents (FBA)	T1: 292
3.	1	Theory of FBA	T1: 293
4.	1	Applications of FBA	T1: 293-296
5.	1	Identification of dyes on fibres	T2: 164-168
6.	2	Estimation of dyes on fibres	T2: 164-178
7.	2	The action of light on dyes	T2: 223-226
8.	2	The action of light on fibres	T2: 223-226
9.	2	Fading action mechanism	T2: 226-230
10.	1	Revision and discussion of important questions	
11.	1	Discussion of ESE question paper	
12.	1	Discussion of ESE question paper	
13.	1	Discussion of ESE question paper	
	Total No of Hours Planned For Unit V = 17		

T1: Tyagi O.D & Yadav M (2012), A textbook of synthetic dyes. Anmol publications Pvt ltd, New Delhi.

T2: K. venkatraman (1952), the chemistry of Synthetic dyes, Part I, Academic press, New York.

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1. K. Venkataraman, The chemistry of synthetic dyes Part I & II, Academic Press, New York, 1952.
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UNIT - I

SYLLABUS

Colour and chemical constitution Colour and chemical constitution - chromophore, auxochrome and resonance, various theories; History of natural and synthetic dyes; Names of commercial dyes; Study of raw materials and dyestuff intermediates; Unit operations - nitration, sulphonation, halogenation, amination, diazotisation and alkali fusion; Classification of dyes based on chemical constitution.

DYES

(i) A dye or dyestuff may be defined as a coloured organic compound which is used for imparting colour to a substrate.

(ii) Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance.

(iii) The dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied.

(iv) Usually, the substrate is the textile fibre or fibre or fabric. In addition to these, there are other substrates like as paper, leather, plastics, wax, cosmetic base, etc. the non-toxic dyes are used for colouring the food stuffs and drugs. The colour sensitive dyes are used in colour photography.

(v) The color intensity of the dye molecule depends on how strongly it absorbs radiation in the visible region, which extends from 400 to 700 nm.

(vi) A dye is a coloured substance whereas all coloured substances are not dyes. Thus a dye should fix itself on the substrate to impart it a permanent coloured appearance.

(vii) For example, azo benzene is not a dye even if it is red in colour, as it cannot be attached to substrate. However, Congo red is a dye because it can be applied on cotton and retained by it. Thus, the dyes should have certain groups which help the attachment of the fibre.

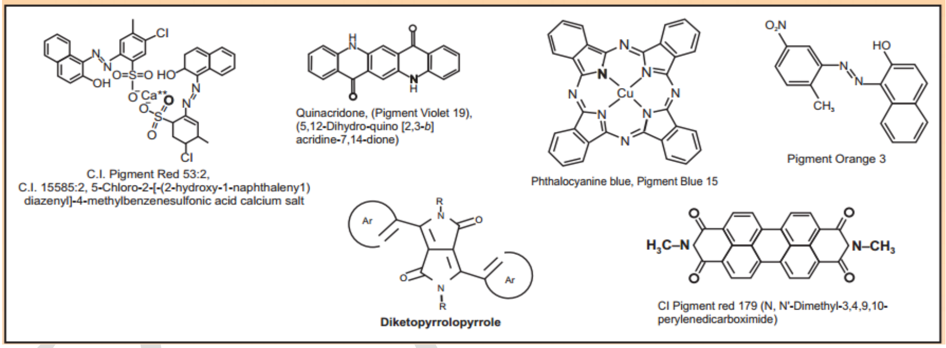
PIGMENT

(i) It is the coloured substance which is insoluble in water or other solvents. It means that the application of dye and pigment will be different.

(ii) A dye is applied in the form of a solution, while the pigment is applied in the form of a paste in a drying oil, in which it is insoluble.

(iii) Pigments both inorganic and organic types, are almost always applied in an aggregated or crystalline insoluble form that requires a binder to form a coating on the surface of a substrate. Pigments do not interact with the substrate and hence do not destroy the crystal structure of the substrate

(iv) There are some colourless compounds which are used as the optical brighteners. They are also known as the white dyes. They have the special property of absorbing ultraviolet light and re-emitting the visible light so that the fabric appears bright.



Structure of Dyes & Pigments

Chromophore

The partial structures necessary for color (unsaturated groups that can undergo π-π* and n-π* transitions) were called chromophore. C=C, C_6H_6, N=N, $-NO_2$, C=O, -CHO groups are examples for chromphores

Auxochromes

It was also observed that the presence of some other groups caused an intensification of color. These groups are called *auxochromes*. The auxochromes are groups that cannot undergo π-π* transitions, but can undergo transition of n electrons: -OH, -OR, -NH2, -NHR, -NR2, -X

Basis for color

Unlike most organic compounds, dyes possess colour because they 1) absorb light in the visible spectrum (400–700 nm), 2) have at least one chromophore (colour-bearing group), 3) have a conjugated system, i.e. a structure with alternating double and single bonds, and 4) exhibit resonance of electrons, which is a stabilizing force in organic compounds. When any one of these features is lacking from the molecular structure the colour is lost.
Other factors contributing to colour are illustrated.

Wavelength of light absorption versus colour in organic dyes

Wavelength Absorbed (nm)	**Colour Absorbed**	**Colour Observed**
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue-Green	Red
500–560	Green	Purple
560–580	Yellow-Green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-Blue
605–700	Red	Blue-Green

In addition to chromophores, most dyes also contain groups known as *auxochromes* (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility. Figure 1 shows the relationships between wavelength of visible and colour absorbed/observed.

Historical Background

- Up to the middle of nineteenth century, the dyestuffs used for textiles were obtained from natural sources viz. vegetable, animal and mineral sources.
- As these dyes were not simple water-soluble substances, complex procedures were used to give rich and fast (but expensive) colours. The fabrics in Fig. 2.2 have been dyed with vegetable dyes.
- In 1856 a British Chemist named William Henry Perkin, produced a brilliant mauve dyestuff (Fig. 2.3) from coal tar which was the first synthetic dyestuff.
- This led to an understanding of the chemistry of dyes and a number of synthetic dyes were developed with the result that by the end of the nineteenth century, the natural dyes were almost completely replaced by synthetic dyes.
- Interestingly there has been a flow of activity in the recent past relating to the use of natural dyes for colouring textiles.

Some natural dyes and their sources

colour/class	name	source
yellow/flavonoid	weld quercetin safflower	seeds, stems, leaves of *Reseda luteola* North American oak bark, *Quercus tinctoria nigra* dried petals of *Carthamus tinctorius*
red/anthraquinone	kermes cochineal alizarin	insects, *Coccus ilicis* insects, *Dactylopius coccus* madder plant roots, *Rubia tinctorum*
blue/indigoid	indigo, woad	indigo plant leaves, *Indigofera tinctoria L.*
purple/indigoid	Tyrian purple	mollusks, *Murex brandaris*
black/chroman	logwood	heartwood, *Haematoxylon campechianum L.*

- Until the 1850s virtually all dyes were obtained from natural sources, most commonly from vegetables, such as plants, trees, and lichens, with a few from insects. Solid evidence that dyeing methods are more than 4,000 years old has been provided by dyed fabrics found in Egyptian tombs. Ancient hieroglyphs describe extraction and application of natural dyes. Countless attempts have been made to extract dyes from brightly coloured plants and flowers; yet only a dozen or so natural dyes found widespread use. Undoubtedly most attempts failed because most natural dyes are not highly stable andoccur as components of complex mixtures, the successful separation of which would be unlikely by the crude methods employed in ancient times. Nevertheless, studies of these dyes in the 1800s provided a base for development of

Raw Materials Used for Dyes

- Dyes used in textiles are used to color the original raw material and therefore product. Dyes can be synthetic, which means they are scientifically made with chemicals, or natural. Dyeing is usually processed into textiles through a combination of water and the synthetic or natural dyes.
- Natural dyes are made from plants and minerals, then are combined with starches and seaweed to make sure it takes to the material.
- Synthetic dyes are usually made from coal tar and petroleum.
-

Raw Materials Used in the Textile Industry

Cotton, Wool, Silk

According to their nuclear makeup, dyes can be anionic or cationic. Some types of synthetic dyes include:

- Acid - Acid-based dyes are used mostly on nylons and wool.
- Sulfur - These dyes are combines with caustic soda and water to color clothing, but they lighten quickly.
- Reactive - These dyes only dye clothing as a reaction to certain fibers, and are best used on silk, wool, and acrylics.
- Azoic - Lighter coloring dyes that fade quickly but are cheap to use.
- Oxidation - These dyes start off without color and are combined with specific chemicals to create new colors. This type of dye is used a lot for hair coloring.

- Mordent - This is a chrome based dye that has to be blended with different types of acid to color wools and cotton.
- Solvent - This dye is usually used in organic dyeing processes, because it can be used with organic compounds.
- Vat - These dyes require four steps of processing, starting off in a vat, and then combined with certain chemicals.

Dyestuff intermediates

- Dyes and dye intermediates industry is an important sector of the Indian chemical industry. This sector has grown at a very fast pace after independence and nearly half of its production is being exported today.
- There is emanating of wastewater from the various operation of the plant. The quantities of effluents generated from various units. The effluents generated during the operations are mainly from washing and utilities. The pollution that accompallles this industry, its nature and extent is, particularly, because of the non-biodegradable nature of the dyes as well as due to the presence of acid/ alkali/ toxic trace metals/ carcinogenic aromatic amines in the effluents.
- The wastewater generated from dye and dye intermediate industries, mainly have intense colour having various shades like red, blue green, brown and black through the production of different colour containing dyes and usually have high level of COD, BOD, acidity, chlorides, sulphates, phenolic compounds and various heavy metals viz. copper, cadmium, chromium, lead, manganese, mercury, nickel, zinc etc.
- Dyes, as they are intensively coloured, cause special problems in effluent discharge and even small amount is noticeable. The effect is aesthetically more displeasing rather than hazardous, and can prevent sunlight penetration decreasing photosynthetic activity in aquatic environment. Although, some azo dyes that cause theeffluent colour, have been implicated as being mutagenic/ carcinogenic as well as toxic to aquatic life.

Classification of dyes based on chemical constitution

Vat Dyes

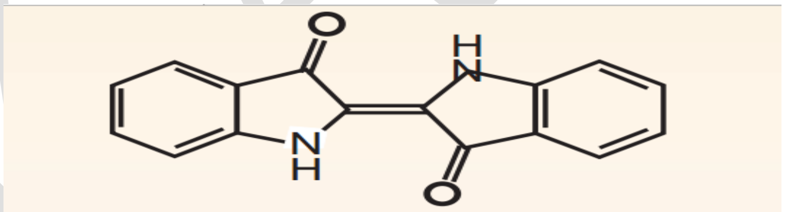
Vat dyes are insoluble organic compounds and do not have any substantively to cellulose. These dyes are widely used for cellulose fibers and can also be used for protein and nylon fibers. They produce good color range but limited selection of orange, blue. Bright green are more popular in this class. Large amount of dyes are required to attain deeper shade.

Application

Since these dyes are insoluble in water, it can not be applied directly to the fabrics. First these dyes are converted into water soluble form, by reducing it with the help of Caustic soda and Sodium hydro sulphite.

When these dyes become soluble in water, they can be applied on a fabric. After the application, these dyes are again converted into water insoluble form by oxidation process, with the use of hydrogen peroxide and acetic acid or simply by air oxidation.

- These dyes are most difficult to process and require a skilled person to dye the fabric.
- Vat dyes have excellent fastness to crocking, perspiration, chlorine bleaching, oxidizing agents and high temperature treatments.



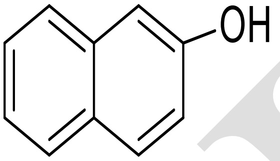
Indigo, (2, 2'-Bis
(2, 3-dihydro-3-oxoindolyliden). Indigotin

Structure of Indigo Dye

This is a very expensive dyeing process and high initial cost of dye and chemicals prevent it from uses in normal fabrics dyeing. Vat dyes are used on best quality of the fabricswhere all round fastness is required. Indigo is the first known class of Natural Vat dye.

Azoic/Napthol Dyes

Azoic Dyes are derived from aryl amides organic compounds. These chemical compounds cannot be used directly as dyes. However, the dyes are formed inside the fibre by the reaction of primary Amines with Napthols, under controlled conditions. Hence, these dyes are also called ingrain dyes. Azo group is generally present in this class of dyes, so it is also called Azo dyes. These classes of dyes are also insoluble in water and primarily used for cellulose fibre. Some times these are used with triacetate to produce black shades. These dyes produces full range of red , orange, brilliant yellowcolour along with maroons, scarlet, deep black and burgundies. Azoic dyes lack green and bright blue colors.



2 - Napthol, DiazoCoupling Component

Structure of Azoic Dye

Application

These dyes are applied in two stages; first stage is called Naptholation of the fabric. In the second stage, the fabric is treated with soluble salt of primary amines, at cold condition, generally 0°C – 5°C. Hence these dyes are also called Ice colour. Due to this, these dyes are the first choice of the dyers for Batik printing. These dyes have good color fastness to washing and dry cleaning and poor to good fastness to light. Dark colors have poor fastness to crocking. Azoic Dyeing process is complex and time consuming.

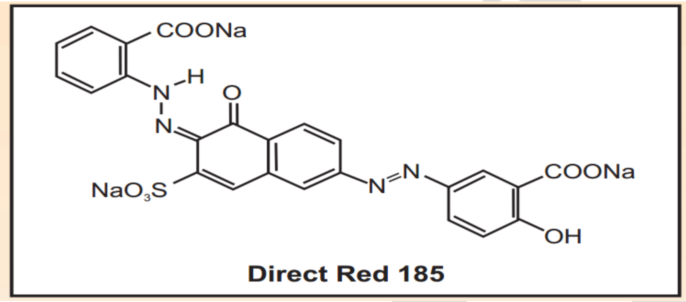
Direct Dyes

These dyes are derived from a formulation of Benzedrine salts. These are water soluble dyes and least expensive one. These dyes are easy to apply and can be applied directly on the fabric, without any pretreatment. Dye fixing agents are not required to fix this category of dye. These dyes are widely used on cellulosic fibers.

Application

These are water soluble dyes; hence, can be directly applied on the fabric. These dyes have good color fastness to perspiration and dry cleaning. Light fastness of these dyes varies widely from poor to very good.

Some direct dyes are metalized with copper to increase their light fastness. In other cases, copper salts are applied as an after treatment for improving light and wash fastness. These dyes have poor fastness to washing and crocking. Majority of the direct dyes are used as back ground color for discharge printing.



Structure of Direct Dye

Sulfur Dyes

These dyes are derived from the formulation of compounds containing sulfur. These are water insoluble dyes and applied by exhaust dyeing method. Sulfur dyes are widely used for cellulosic fibres for darker shades

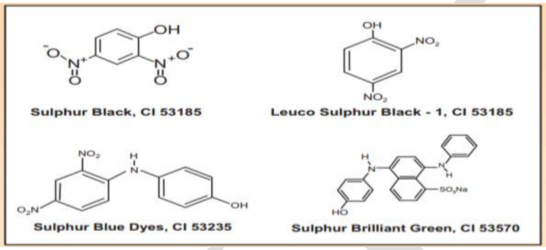
Application

These are water insoluble dyes, and cannot be applied on fabric directly. Sulfur dyes are made water soluble by reducing with Sodium Sulphite and sodium hydroxide. If dye are still insoluble than small amount of Sodium Hydro Sulphite is added with warm water. Once the dye becomes water soluble, it is applied by exhaust dyeing method.

After completion of dyeing, Sulfur dyes are again converted into water insoluble by oxidation process. These dyes are generally used for darker shades especially Navy blues, Jet black, Brown and Khakhi colors. These dyes are not having full spectrum of colors, true yellow color is not available in this dye category.

Properties

Sulfur dyes are relatively easy to dye cellulosic fibre with good-to-excellent washes and lights fastness at a low cost. It produces a complete range of colors in “dull shade” and gives poor light fastness in pastel shades. These dyes are mainly used for dyeing black, brown, navy blue or olive, in medium to dark shades. Some yellows and blues shades are also available but there is only one red and a green dye



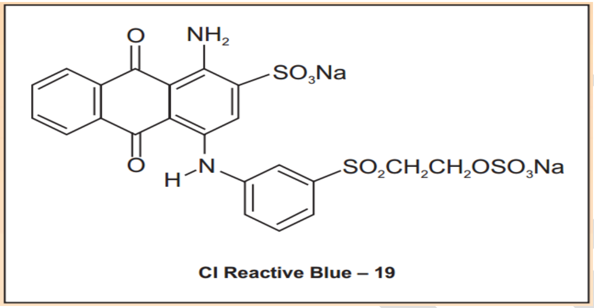
Structure of Sulfur Dyes

Sometimes, these dyes are also used for improving the wash fastness of the Direct dyed fabric called topping. Sulfur dyes are having good fastness to light, washing, dry cleaning and perspiration. However, these dyes have poor fastness to chlorine bleach. Sulfur dyed materials cannot be stored for longer periods at higher than normal room temperature because in presence of moisture , It tends to oxidize and form sulfuric acids, and then this acid cause tendering to cellulose fabric. Due to this tendering process, sometimes the color of the fabric also changes and become dull. This is called bronziness of the shade.

Reactive Dyes

Reactive dyes are water soluble dyes, which are anionic in nature. Since these type of dyes react with fibers and make covalent type of bonding with the fiber, hence they are called Reactive dyes. These dyes can be classified as hot brand reactive dyes and cold brand dyes. Procion (Triazine type)-H, is a hot type of reactive dye and it react with cellulose in presence of sodium carbonate at the temperature range of 75-90°C. Procion-C is cold type of reactive dyes, reacts at room temperature in presence of sodium carbonate. Ramazol is another type of reactive dyes (Vinyl sulfone reactive dye) and react in presence of base and under goes elimination reaction to form vinylsulfone group, which then combines with cellulose and make bonding. It is a time consuming process.

These dyes are primarily used for cotton and other cellulose ¿ber at an alkaline pH of 9-12. However, these dyes can also be used for wool, silk and polyamide ¿bers in weak acidic dye baths.



Structure of Reactive Dye

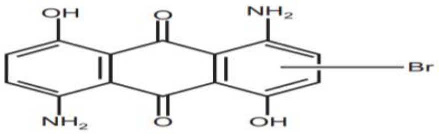
Application

Reactive dyes can be applied by exhaust method, as well as pad batch method also. Reactive dyes are available in complete range of colors. They are very bright incolors.

- These dyes are having very good fastness to washing, Good-very good fastness to light, Good fastness to dry cleaning, perspiration, crocking and poor fastness to chlorine bleaching.
- It is very easy to obtain level dyeing using reactive dyes. These dyes are having high flexibility in the choice of method of application of dyeing.
- Cost of using reactive dyeing is high, because of price, loss of dyes during application and extensive washing. These dyes take excessive time for the dyeing process.

Disperse Dyes

These dyes were originally developed for the dyeing of cellulose acetate but now a days, they are used to dye nylon, cellulose triacetate and acrylic fibres too. These dyes were largely used for dyeing of polyester material. Disperse dyes are Non-ionic aromatic compounds with relatively low molecular weight and has an extremely low solubility in water. These dyes are available in the form of powders, granular, liquid or paste form. These dyes can be sublimize at higher temperature and this sublimation properties of Disperse dyes at high temperature is used in the transfer printing and rapid dyeing process. Dyeing of polyester is generally carried out at high temperature and high pressure. These dyes are also used for heat transfer printing. Disperse dyes produces very good range of shades except dark blue and black. These dyes are having good -excellent fastness to perspiration, crocking and dry cleaning and Fair-Good fastness to light and washing. When these dyes are used on acetate, it exhibit poor fastness to light and subject to gas fading.

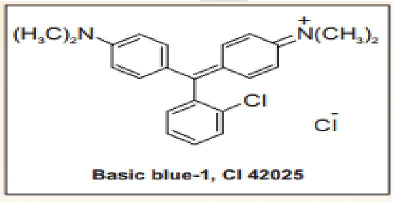


CI Disperse Blue 56

Structure of Disperse Dyes

Basic Dyes

Basic dyes are derived from salts of tri phenyl methane derivatives. These are water-soluble dyes and contains cationic group. These dyes are mainly used for dyeing of acrylic and mod acrylics materials. Apart from these, basic dyes can also be used for effectively dyeing of wool and silk but with poor fastness properties. It can also be used for dyeing of nylon. Some variety of polyester can also be dyed with Basic class of dyes. A basic dye produces complete range of bright color with Good color fastness to light, washing, perspiration and crocking for acrylic and mod acrylic. However, it exhibit very poor fastness to washing and light on wool and silk.

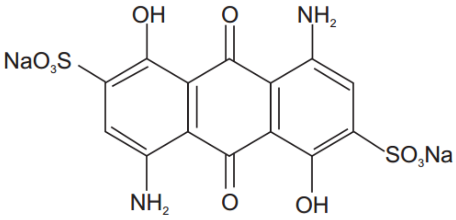


Basic blue-1, CI 42025

Structure of Basic Dyes

Acid Dyes

These dyes are sodium salt of sulphonic acid that are having very good affinity to wool and silk fibre under acidic medium. These dyes are available in a form of salts and are watersoluble. These dyes are applied in acid medium by exhaust method. Acid dyes are mainly used for dyeing of wool and silk. However, Acrylic, nylon and spandex can also be dyed with acid dyes with excellent fastness properties. An acid dye produces complete range of color except bright red and greenish blue. However, some of the bright colors tend to bleed while some colors have good colorfastness to light, dry cleaning and crocking. Few of the Acid dye have poor fastness to washing.

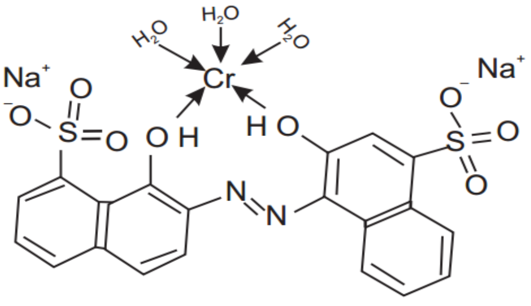


CI Acid Blue 45

Structure of Acid Dyes

Chrome / Mordant / Metallic Dyes

- In this class of dyes, Metallic salt of cobalt’s, aluminum or copper are added to dye molecules for improving fastness properties of the dyes. These dyes are generally water soluble in nature and are applied in acidic medium. Mordent dyes takes more time compare to other class of dyeing. These dyes can beapplied in fiber, yarn or fabric form.
- Metallic dyes are effectively used for dyeing of wool & silk, where maximum wet fastness is required. However, Acrylic, nylon, and spandex can also be dyed with mordent dyes.
- Mordent dyes have excellent fastness to perspiration and washing. Good fastness to light and dry cleaning and very good fastness to crocking.



Acid Blue 158 Pre metallized Acid dyes

Structure of Metallic Dyes

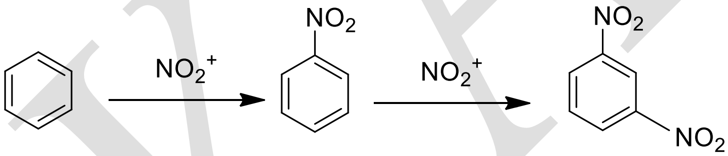
NITRATION

$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$

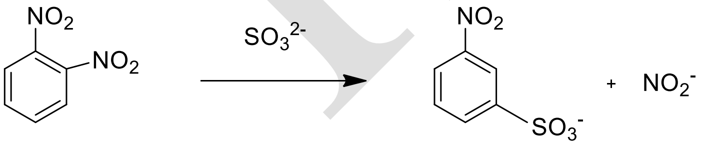
$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O+ + 2HSO_4^-$

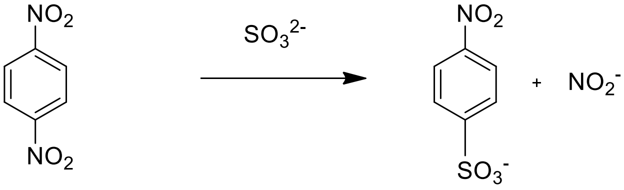
Preparation of nitro compounds used in dyestuff industries

1. **m-Dinitrobenzene**

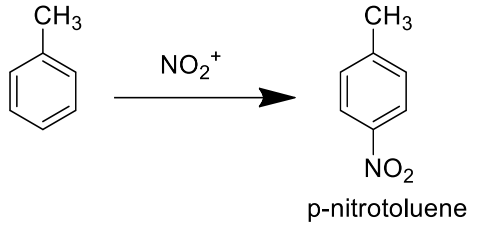


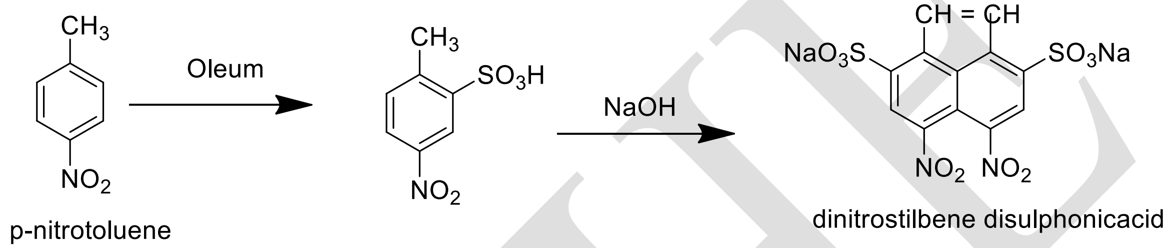
m-dinitrobenzene





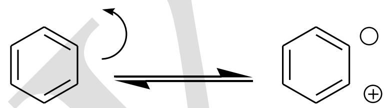
2. p-Nitrotoluene

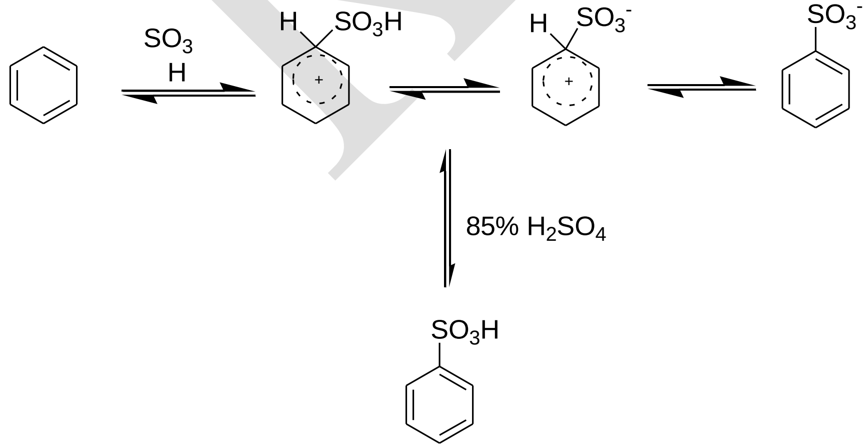




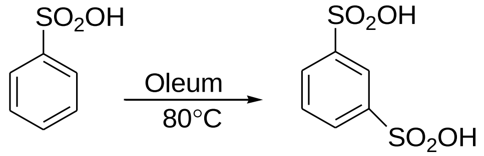
Sulphonation

$$2H_2SO_4 \rightleftharpoons H_3O_+ + HSO_4 + SO_3$$



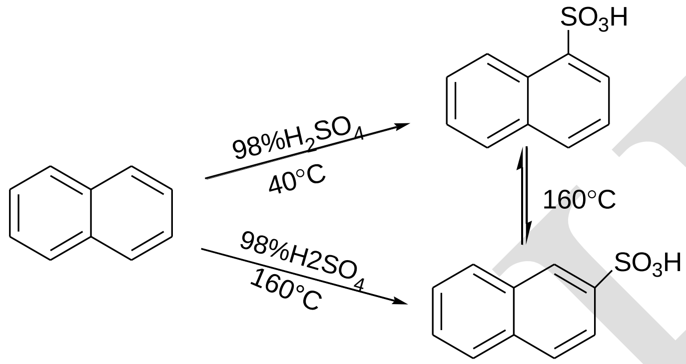


Sulphonation of Benzene:

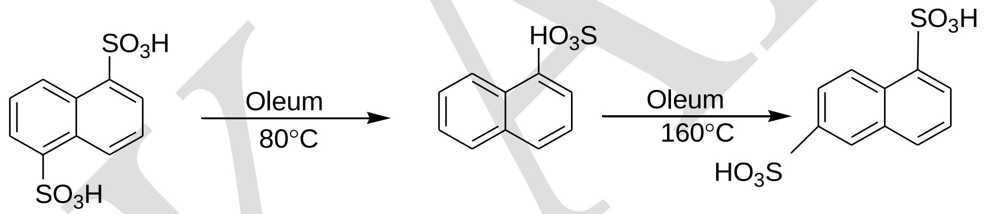


Sulphonation of Naphthalene:

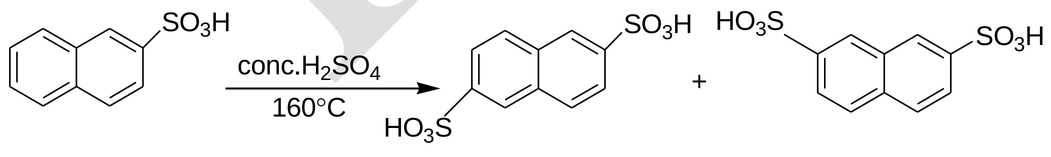
(a)Naphthalene-1-Sulphonic acid



Naphthalene-1,5disulphonic acid Naphthalene-1,6-disulphonic acid

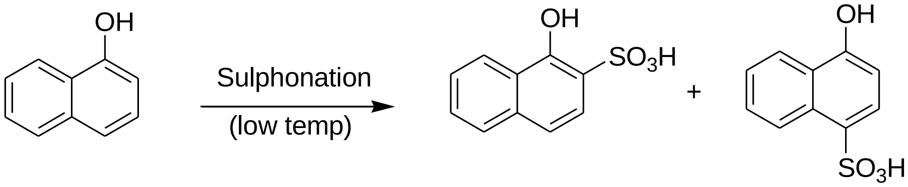


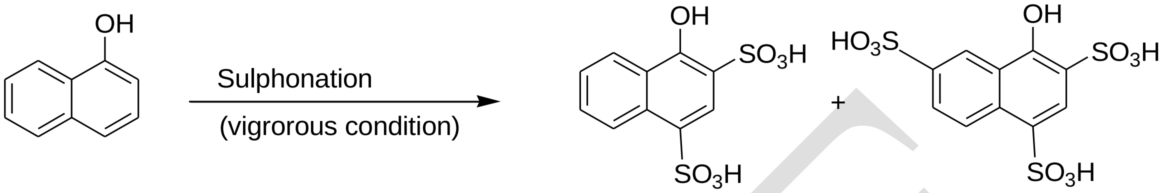
Naphthalene -2, 6-disulphonic acid and Naphthalene -2,7-disulphonic acid.



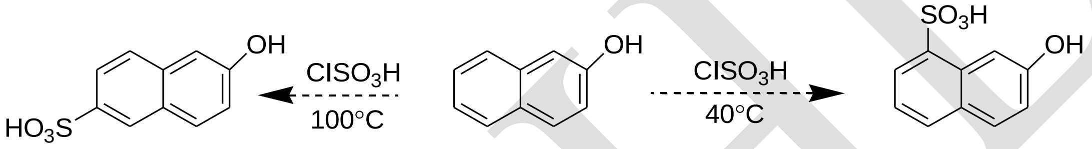
Sulphonation of Naphthol

(a)Sulphonation of α-naphthol or 1-naphthol.





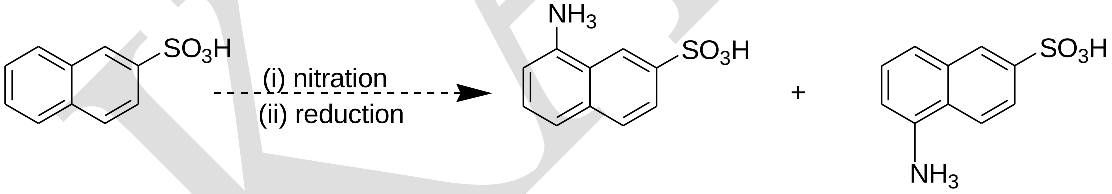
(b)Sulphonationof β-naphthol or 2-naphthol



Naphthylaminesulphonic acids

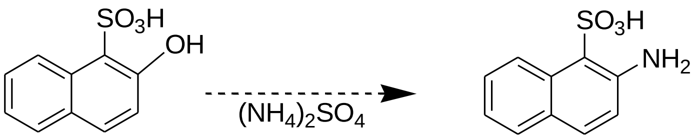
(i)α-Naphthylaminesulphonic acids

(b)α-Naphthylamine-6-sulphonic acid and α-Naphthylamine-7-sulphonic acid.

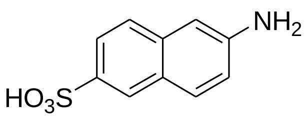


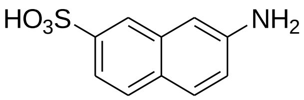
(ii)β-Naphthylaminesulphonic acids

(a)β-Naphthylamine 1-sulphonic acid (to bias acid).

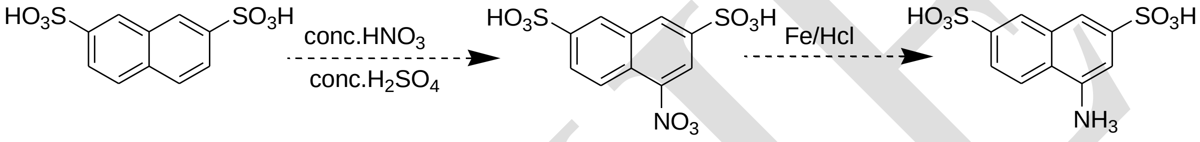


(b)2-Naphthylamine 6-sulphonic acid or bronner acid and 2-Naphthylamine -7-sulphonic acid or Cassella acid

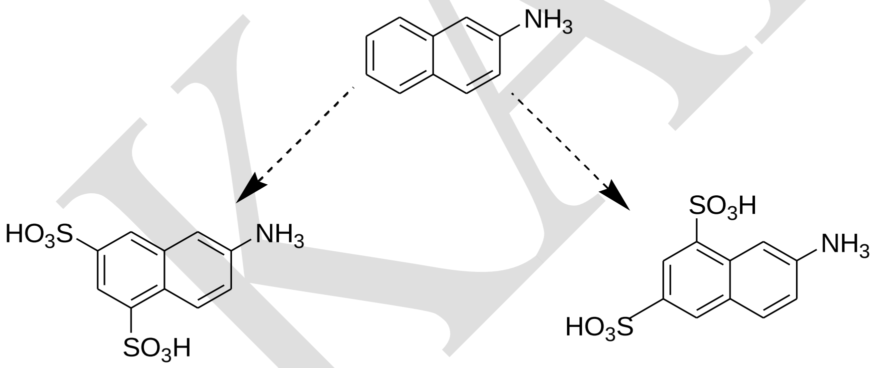




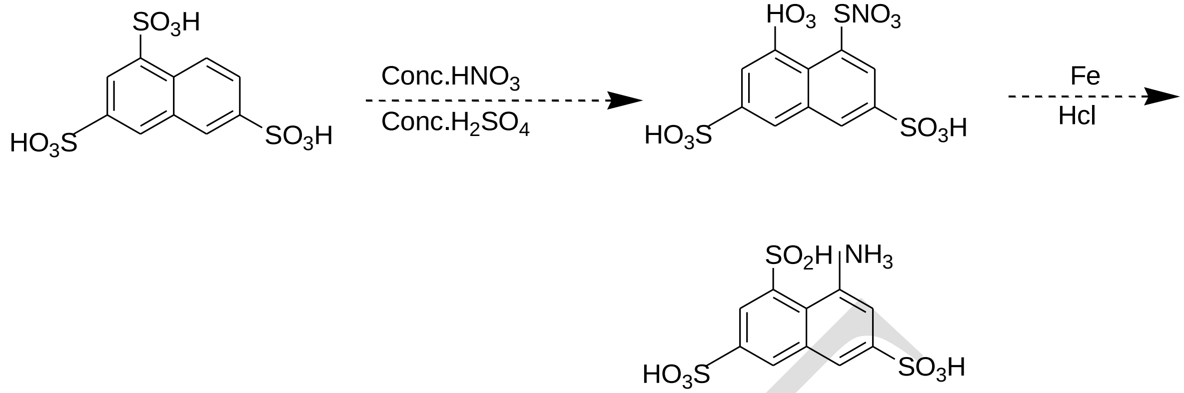
(c)α-Naphthylamine -3-disulphonic acid *(Freund acid)*.



(d)β-naphthylamine-6, 8-disulphonic acid (Amino G-acid)

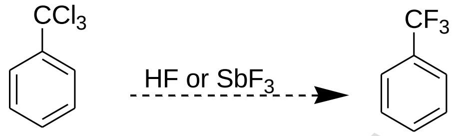


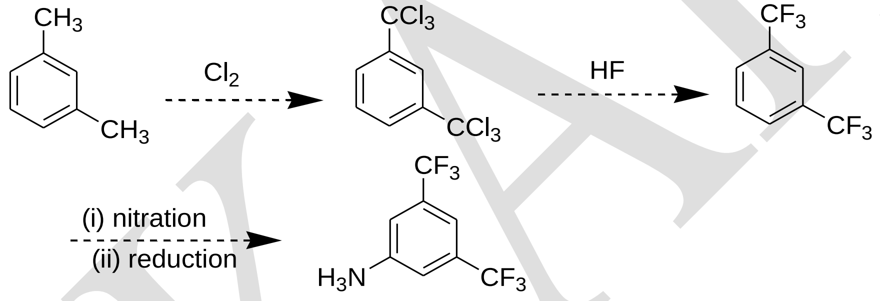
(e)α-Naphthylamine-3, 6, 8-trissulphonic acid (Koch Acid).



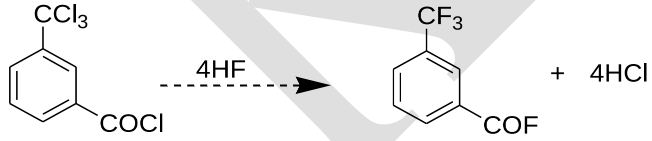
Halogenation

(i) Fluorination



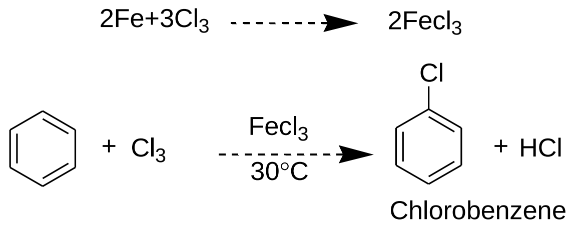


Fast orange GGD base

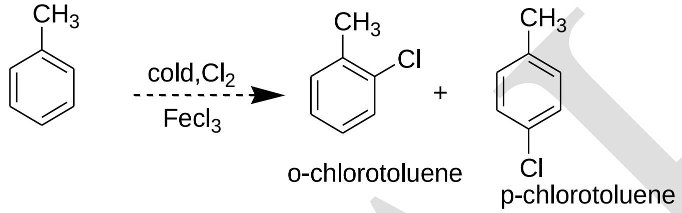


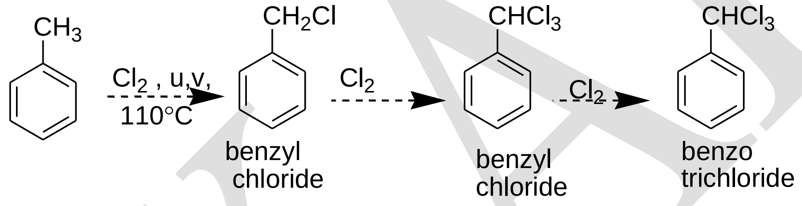
Chlorination

chlorination of Benzene

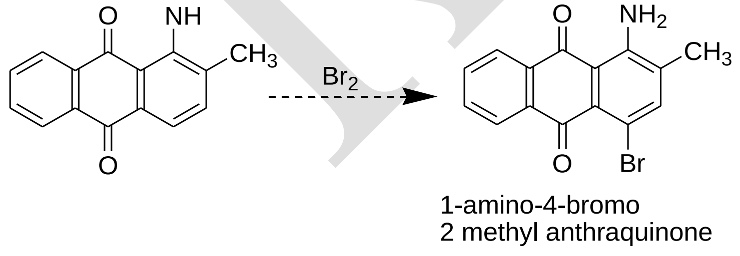


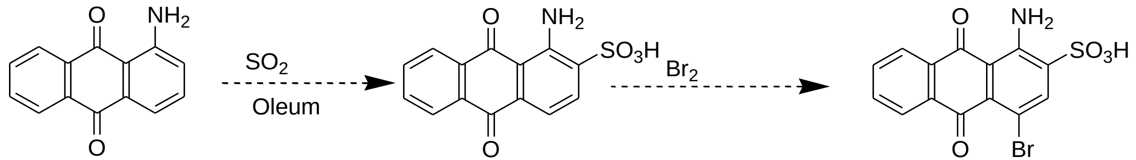
Chlorination of toluene.





Bromination



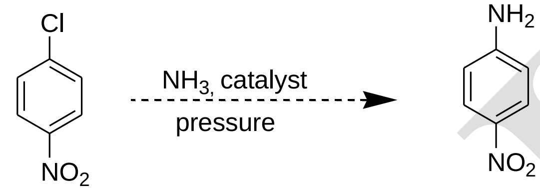


1-aminoanthraquinone

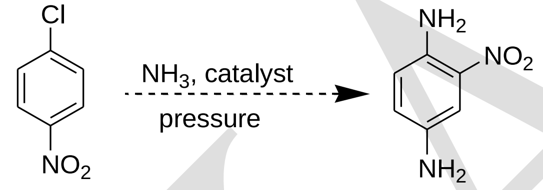
1-amino-4 bromo anthraquinone
2 sulphonic acid.

Amination

(i)Amination of Benzene Derivatives.

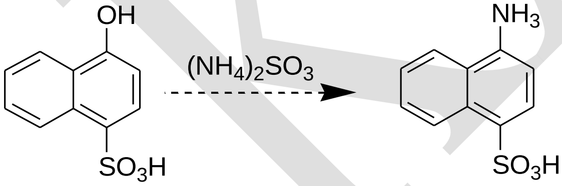


p-chloronitrobenzene p-Nitroaniline



2,4-Dinitrochlorobenzene 2,4-Dinitroaniline

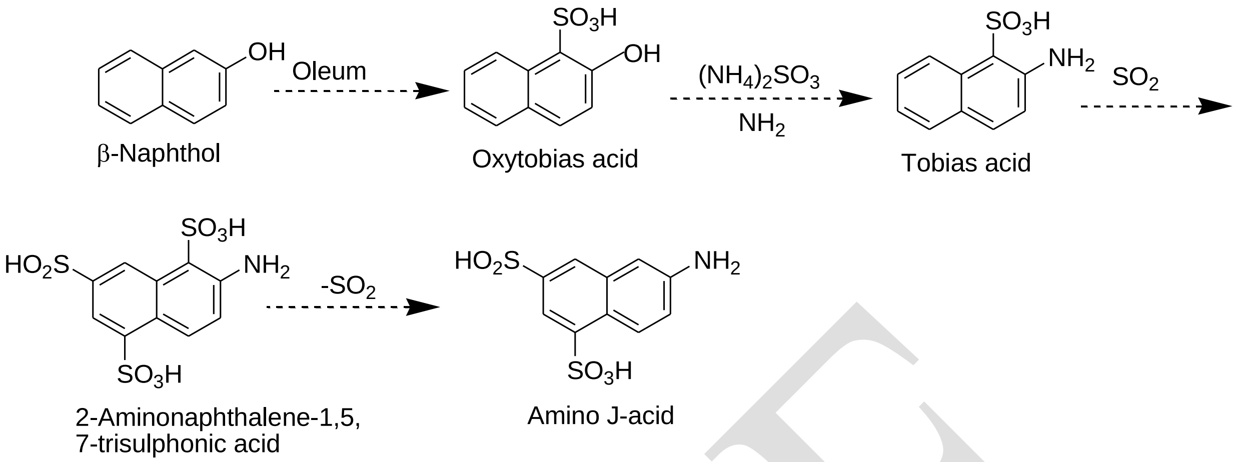
(ii) Amination of Naphthalene Derivatives.



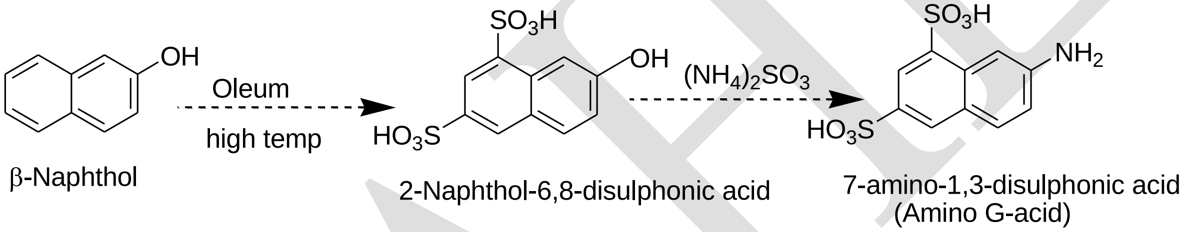
α-Naphthol-4-
sulphonic acid

1-Amino naphthalene
4-sulphonic acid
(Naphthonic acid)

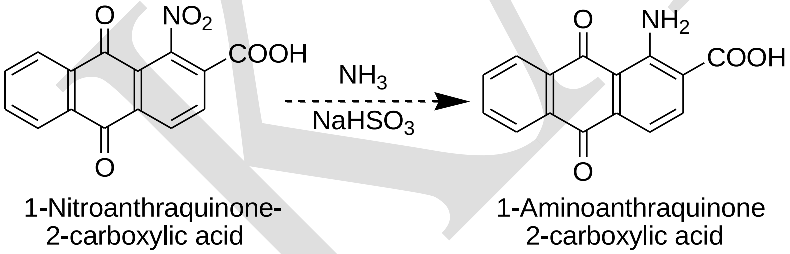
Synthesis of J-acid.



Synthesis of Amino G-acid.



Amination of anthraquinone.



POSSIBLE QUESTIONS

PART – B (5 X 8 = 40 MARKS)

1. Explain in detail about Chromophore, Auxochrome and Resonance
2. Give a detail account on Nitration reaction with examples
3. Write the difference between Dyes and Pigments
4. Give a detail account on History of natural and synthetic dyes
5. Explain the mechanism of Sulphonation reaction with examples
6. Discuss the classification of dyes based on chemical constitution
7. Describe in brief colour and chemical constitution of dyes
8. What is amination? Explain its mechanism and describe amination of one aromatic molecule
9. Explain the structure and reactions of some commercial dyes
10. what is diazotization? Explain its mechanism in detail

UNIT I

Questions	A	B	C	D	ANSWER
The naphthylurea dyes (XII) were noted to possess an average fastness of ……….	Two- three	three-five	five-six	six-ten	**two-three**
Most preformed ……………………. dyes produce dyeings of high lightfastness on wool	metal	metal-complex	ligand	caarbon	**metal-complex**
……………………..substituted dyes will possess no inherent surface activity	symmetrically	asymmetrically	geometrically	optically	**symmetrically**
Chromogen is the aromatic structure containing ……………………rings.	Benzene	alipahtic	methane	heterocyclic	**Benzene**
A chromophore is part or moiety of a molecule responsible for ………….	rings	colour	wool	dye	**color**
………are added to a structure, the energy required to reach the first excited state decreases	single bonds	symmetry	conjugated double bonds	alipahtic	**conjugated double bonds**
Dye containing one azo group is called a ……..	double	triple	monoazo dye	couple	**monoazo dye**
Mauveine was discovered by ……..	newton	chadwik	alferd	William Henry Perkin	**William Henry Perkin**
……… dyes are used for dyeing animal or vegetable fibers	direct	acid	reactive	basic	**direct**
……… are mainly used for dyeing wool.	Acid dyes	direct dyes	reactive dyes	vat dyes	**Acid dyes**
…….. dyes are essentially insoluble in water	Acid dyes	direct dyes	reactive dyes	vat dyes	**vat dyes**
Disperse dyes are also known as ……….	Acid dyes	acetate dyes	reactive dyes	vat dyes	**acetate dyes**
…………. is the largest selling dye by volume	Sulfur black	acetate dyes	Acid dyes	reactive dyes	**Sulfur black**
India is now the ……………… largest producer of dyes	first	second	third	fifth	**second**
……………… founder of dyestuff industry	Bayer	Hoechst	William H Perkin	hayward	**William H Perkin**
The first sulfur dyes were made from ……….	Amination	Nitration	sulfonation	thionation	**thionation**
…….. is a red dye extracted from the roots of the madder plant.	Alizarin	logwood	Azomethane	Anthaquione	**Alizarin**
……. is the only natural dye used today	Azomethane	Anthaquione	logwood	Alizarin	**Logwood**
Dyes contained conjugated systems of benzene rings bearing simple unsaturated groups are called ……..	Chromophore	Auxochrome	Chromogen	Adsorption	**Chromophore**
The combination of specific chromophore-auxochrome are termed as………		chromogen			**chromogen**
The colours of dyes and pigments are due to the absorption of ………. by the compounds	X-ray	sunlight	visible light	IR	**visible light**
Human eyes detect radiation over only the small visible range of ……….	200-800	400-800	100-1000	400–700 nm.	**400–700 nm.**
Synthetic dyes tend to give…….. colours	brilliant	Dark brown	yellow	red	**brilliant**
…… molecules are polymeric chains of repeating units of five major chemical types	benzene	Fibre	nano	crystals	**Fibre**
………. is colourless in acid and intensely red in base	methyl red		phenolphthalein		**phenolphthalein**
……………. is a red dye used for paper, inks, and cosmetics	vat	resin	Tetrabromofluorescein	carbon	**Tetrabromofluorescein**
…….. Is used for dyeing silk	thiazines				**thiazines**
……………..is widely used as a biological stain		Methylene blue			**Methylene blue**
……………. are good leather dyes			oxazines and acridines		**oxazines and acridines**
……. dyes became the most important commercial colorants.	Azo	vat	resin	acid	**Azo**
……………. dyes were used to obtain bright blue shades	benzene	aliphatic	anthraquinone	methanol	**anthraquinone**
The azo dye amaranth was banned in……	1976	2000	1940	1932	**1976**
Azo dyes contain at least……….. attached to one or often two aromatic rings.	one azo group	two azo group	three azo group	four azo group	**one azo group**
Basic dyes are……… and produce colored cations in solution	oil soluble	water-soluble	paste	metals	**water-soluble**
The auxochromes are groups that cannot undergo ……..transitions.	π-π*	n- π	π- π	non-bonding	**π-π***

The combination of specific chromophore-auxochrome are termed as	chromogen	nylon	wool	scouring	**chromogen**
1-napthol – 2 – sulphonic acid is also called as ………………	Schaeffe's acid	Nevile – Winther's acid	Tobias acid	Cassella acid	**Schaeffe's acid**
The process of introducing of an amino group in an aromatic nucleus is known as ……..	Nitration	Sulphonation	Acylation	Amination	**Amination**
…….is the leading fibre in Textile Industry.	nylon	Cotton	wool	wood	**Cotton**
……….of cotton textiles is an essential treatment in textile.	Packing	Scouring	grinding	welding	**Scouring**
Dyes are normally ……..soluble	oil	water	acid	crude	**water**
……..donot interact with the substrate.	complex	chemicals	Pigments	dyes	**Pigments**
……. may be classified according to their chemical structure.	Dye	Direct	Acid	Vat	**Dye**
……….acid dyes are used mainly on wool for improved fastness.	methane	benzene	organic	Metal complex	**Metal complex**
Dyes are ……..which are widely used for imparting colour to textiles.	inorganic compounds	organic compounds	physical	Vat	**organic compounds**
…….is the leading fibre in Textile Industry.	nylon	Cotton	wool	wood	**Cotton**
………..is the solubilisation of insoluble protopectin and give rise to highly polymerized soluble pectin.	protein	Protopectinases	Vitamin	Fibre	**Protopectinases**
……….of enzyme molecule on to the substrate surface.	absorption	sorption	emission	Adsorption	**Adsorption**
……..are soluble in water and are applied under acidic conditions.	acid dye	vat dye	Direct dye	Fibre	**acid dye**
Dyes effluent is largely ……..and coloured in nature.	physical	organic	inorganic	nano	**inorganic**
The textile industry accounts for the largest consumption of …….	organic	inorganic	oil	dyestuffs	**dyestuffs**
Nitration reaction carried out by the mixture of ………………..	Con. HCl + Con. HNO_3	Con. HCl + Con . H_2SO_4	Con. HNO_3 + Con . H_2SO_4	Con. H_2SO_4 + CH_3COOH	**Con. HNO_3 + Con . H_2SO_4**
……… and ………. is used as first and end component for the preparation of azo dyes.	Tobias acid and Cassella acid	Bronner acid and Cassella acid	Cleve acid and Bronner acid	Bronner acid and Tobias acid	**Bronner acid and Cassella acid**
Oxidation of anthracene with air in presence of V2O5 leads to the product of ………….	Anthraquinone	Anthraquinone - 2 - sulphonicacid	2-Hydroxyanthraquinone	1-Nitroanthraquinone	**Anthraquinone**
………….derived from a formulation of Benzedrine salts	acid dye	vat dye	Direct dye	Fibre	**Direct dye**
………….are insoluble organic compounds and do not have any substantively to cellulose.	Vat dyes	acid dye	Direct dye	Fibre	**vat dyes**
………………..are combines with caustic soda and water to color clothing, but they lighten quickly.	Vat dyes	Sulfar dyes	Direct dye	acid dye	**Sulfar dyes**
……………..are usually made from coal tar and petroleum.	Synthetic dyes	Sulfar dyes	Direct dye	acid dye	**Synthetic dyes**
…………. are derived from aryl amides organic compound	Azoic Dyes	vat dye	Sulfar dyes	Direct dye	**Azoic Dyes**

UNIT - II

SYLLABUS

Direct, Acid and Basic Dyes - Direct cotton dyes (substantive dyes) – Classification, properties, structure and mechanism of dyeing, post treatment of dyeing.
Acid dyes and Basic dyes – Classification, Characteristics, Mechanism of dyeing, Nature of affinity on cellulose and protein fibres.

Acid Dyes

A class of dyes used on wool, other animal fibers, and some manufactured fibers. Acid dyes are seldom used on cotton or linen since this process requires a mordant. Acid dyes are widely used on nylon when high wash fastness is required. In some cases, even higher wash fastness can be obtained by after treatment with fixatives.

Natural Dyes

Direct Printing, it is the most common approach to apply a color pattern onto a fabric. If done on colored fabric, it is known as overprinting. The desired pattern is produced by pressing dye on the fabric in a paste form. To prepare the print paste, a thickening agent is added to a limited amount of water and dye is dissolved in it. Earlier starch was preferred as a thickening agent for printing. Nowadays gums or alginates derived from seaweed are preferred as they allow better penetration of color and are easier to wash out. Most pigment printing is done without thickeners because the mixing up of resins, solvents and water produces thickening anyway.

Basic (Cationic) Dyes

Basic dyes are water-soluble and are mainly used to dye acrylic fibers. They are mostly used with a mordant. A mordant is a chemical agent which is used to set dyes on fabrics by forming an insoluble compound with the dye. With mordant, basic dyes are used for cotton, linen, acetate, nylon, polyesters, acrylics and modacrylics. Other than acrylic, basic dyes are not very suitable for any other fiber as they are not fast to light, washing or perspiration. Thus, they are generally used for giving an after treatment to the fabrics that have already been dyed with acid dyes.

Synthetic Dyes

Synthetic dyes are classified based upon their chemical composition and the method of their application in the dyeing process.

Direct (substantive) Dyes

Direct dyes color cellulose fibers directly without the use of mordants. They are used for dyeing wool, silk, nylon, cotton, rayon etc. These dyes are not very bright and have poor fastness to washing although they are fairly fast to light.

Disperse Dyes

Disperse dyes are water insoluble. These dyes are finely ground and are available as a paste or a powder that gets dispersed in water. These particles dissolve in the fibers and impart color to them. These dyes were originally developed for the dyeing of cellulose acetate but now they are used to dye nylon, cellulose triacetate, and acrylic fibers too.

Sulfur Dyes

Sulfur Dyes are insoluble and made soluble by the help of caustic soda and sodium sulfide. Dyeing is done at high temperature with large quantities of salt so that the color penetrates into the fiber. After dyeing the fabric is oxidized for getting desired shades by exposure to air or by using chemicals. Excess dyes and chemicals are removed by thorough washing. These dyes are fast to light, washing and perspiration and are mostly used for cotton and linen.

Pigment Dyes

Although pigments are not dyes in a true sense, they are extensively used for coloring fabrics like cotton,wool and other manmade fibers due to their excellent light fastness. They do not have any affinity to the fibers and are affixed to the fabric with the help of resins. After dyeing, the fabrics are subjected to high temperatures.

Mordant Dyes

The mordant or chrome dyes are acidic in character. Sodium or potassium bichromate is used with them in the dyebath or after the process of dyeing is completed. This is done for getting the binding action of the chrome. They are mostly used for wool which gets a good color fastness after treatment with mordant dyes. They are also used for cotton, linen, silk, rayon and nylon but are less effective for them.

Vat Dyes

Vat dyes are insoluble in water and cannot dye fibers directly. However, They can be made soluble by reduction in alkaline solution which allows them to affix to the textile fibers. Subsequent oxidation or exposure to air restore the dye to its insoluble form. Indigo is the original vat dye. These dyes are the fastest dyes for cotton, linen and rayon. They are used with mordants to dye other fabrics such as wool, nylon, polyesters, acrylics and modacrylics.

Reactive Dyes

Reactive dyes react with fiber molecules to form a chemical compound. These dyes, they are either applied from alkaline solution or from neutral solutions which are then alkalized in a separate process. Sometimes heat treatment is also used for developing different shades. After dyeing, the fabric is washed well with soap so as to remove any unfixed dye. Reactive dyes were originally used for cellulose fibers only but now their various types are used for wool, silk, nylon, acrylics and their blends as well.

Macromolecular Dyes

A group of inherently colored polymers. They are useful both as polymers and as dyes with high color yield. The chromophores fit the recognized CI classes, i.e., azo, anthraquinone, etc., although not all CI classes are represented. Used for mass dyeing, hair dyes, writing inks, etc.

Metallized Dyes

A class of dyes that have metals in their molecular structure. They are applied from an acid bath.

Naphthol Dyes

A type of azo compound formed on the fiber by first treating the fiber with a phenolic compound. The fiber is then immersed in a second solution containing a diazonuim salt that reacts with the phenilic compound to produce a colored azo compound. Since the phenolic compound is dissolved in caustic solution, these dyes are mainly used for cellulose fiber, although other fibers can be dyed by modifying the process. (Also see DYES, Developed Dyes.)

Premetallized Dyes

Acid dyes that are treated with coordinating metals such as chromium. This type of dye has much better wet fastness than regular acid dye. Premetallized dyes are used on nylon, silk, and wool.

Gel Dyeing

Passing a wet-spun fiber that is in the gel state (not yet at full crystallinity or orientation) through a dyebath containing dye with affinity for the fiber. This process provides good accessibility of the dye sites.

Developed Dyes

Dyes that are formed by the use of a developer. The substrate is first dyed in a neutral solution with a dye base, usually colorless. The dye is then diazotized with sodium nitrate and an acid and afterwards treated with a solution of B-naphthol, or a similar substance, which is the developer. Direct dyes are developed to produce a different shade or to improve wash fastness or light fastness.

Azo Dyes

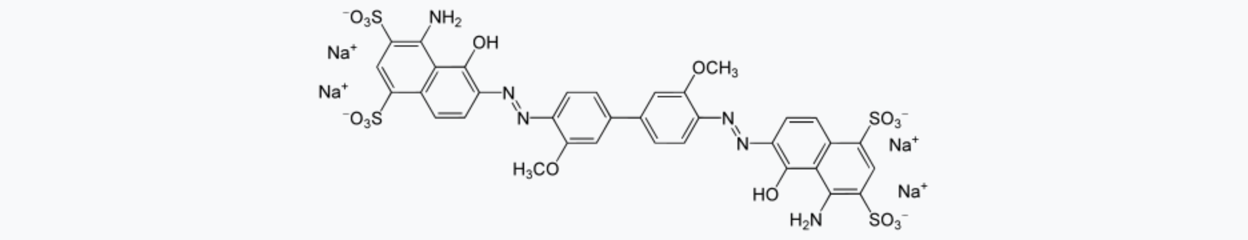
Dyes characterized by the presence of an azo group (-N=N-) as the chromophore. Azo dyes are found in many of the synthetic dye classes.

Definition of DIRECT DYE

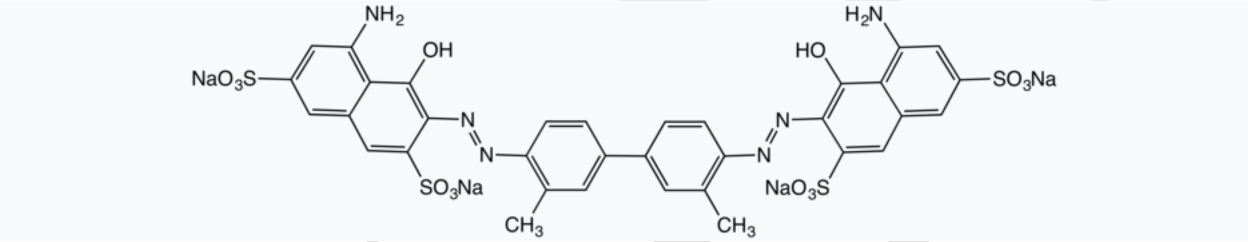
A substantive dye or direct dye is a dye that adheres to its substrate, typically a textile, by non-ionic forces. The amount of this attraction is known as "substantivity": the higher the substantivity the greater the attraction of the dye for the fiber. Substantive dyes work best on textiles with high contents of cellulose, such as cotton. In contrast to direct dyes, wool and leather goods are dyed by the process of ion exchange, exploiting the cationic nature of proteins near neutral pH. The development of substantive dyes helped make mordant dyes obsolete.

Substantive dyes are set in a slightly basic or neutral environment at temperatures close to boiling point. They are set by formation of aggregates of dyes within interstices of the fibres. Aggregation is enhanced by extended aromatic rings.

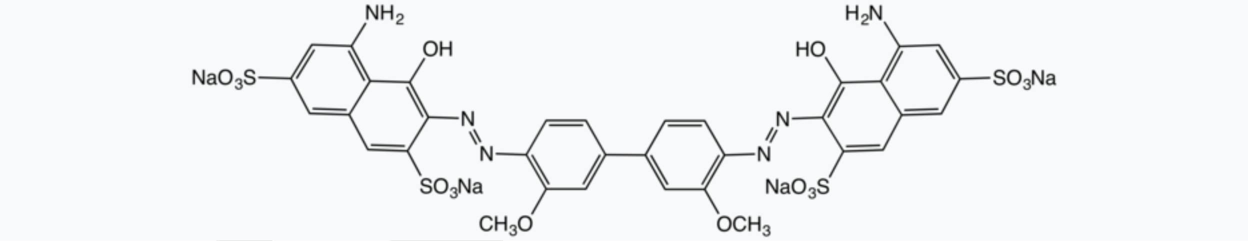
Representative direct dyes



Direct Blue 1.



Trypan blue (Direct Blue 14), which also exhibits medicinal properties.



Direct Blue 15.

A water-soluble dye usually of the azo class that is used in alkaline or neutral solution especially for dyeing cellulosic material (such as cotton or paper) directly

Major types of Direct Dyes

There are two major types of Direct Dyes:

Anionic Direct Dyes

Anionic Direct Dyes are used for coloring papers, controlling tint and shade and correction of two sided paper color. The main structural features of the Anionic Direct Dyes are: the planar vary from each other, the structural single and double bonds are very much extended, and contains one or more than one sulfonate groups. These sulfonate groups make them soluble in the water.

Cationic Direct Dyes

The main structural features of cationic direct dyes are : λ the structural single and double bondings are extended. λ the molecular structure is planar λ positive charges are more than the negative charges

Properties of direct dyes Direct dyes have some characteristics. Followings are tha main properties of direct dyes.

- Direct dyes are water soluble dyes.
- It is anionic in nature.
- It needs electrolyte for exhaustion.
- Dyeing process is carried out in alkaline condition.
- Generally applied for cellulosic as well as protein fibers.
- Fastnees properties are improved by after treatment. λ It is not widely used as compared with reactive dyes.
- Comparatively cheap in price.
- Direct dyes are used for cheap goods for local market.

Chemicals Nature of Direct Dyes Chemically they are salts of complex sulfonic acids. Structure:-More than 75% of all direct dyes are unmetallised azo structures, great majority of them are disazo or polyazo types.

Ionic Nature:-Their ionic nature is anionic.

Solubility:-They are soluble in water .

Affinity:-They have an affinity for a wide variety of fibers such as cotton ,viscose, silk jute ,linen etc.. They do not make any permanent chemical bond with the cellulosic fibers but are attached to it via very week hydrogen bonding as well as vander waals forces. Their flat shape and their length enable them to lie along-side cellulose fibers and maximize the Van-der-Waals, dipole and hydrogen bonds

Dyeing Method The color is pasted well and dissolved in boiling water to get a lump free solution .An addition of 0.5–2 g l–1 sodium carbonate may be advantageous when applying dyes of only moderate solubility in full depths.

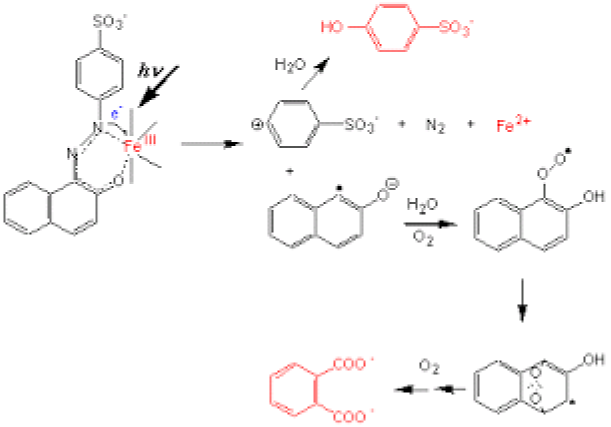
The dye bath is set at 40°C, λ Raise to the boil at 2 degC min–1 Hold at the boil for 30–45 min, λ during hold add 10–15 g l–1 of sodium chloride or calcined Glauber's salt. Light shades are dyed without or lesser addition of salt. λ Improved yields can be achieved when applying full depths by cooling to 80°C at the end of the period at the boil, adding a further 5 g l–1 salt and rising to the boil again

λ Dye bath variables which must be considered for level dyeing, 1.Temperature of Dyeing and rate of heating 2.Electrolyte concentration and addition 3.Time 4.Dye solubility 5.Use of leveling agent

Typical Recipe of Direct Dyeing

Disadvantages of Direct Dyes λ Many Direct Dyes are bland and dull in color. λ Direct Dyes provide duller color than the color provided by the fiber reactive dyes. λ The wash fastness quality is also low. λ Few Direct Dyes have low light fastness.

Mechanism of dyeing



Affinity

It is the difference between the chemical potential of dye in its standard state in the fiber & the corresponding chemical potential in the dye bath i.e. tendency of a dye to move from dye bath into a substance. It is expressed in Joule or cal (per mole) and quantitative expression of substantivity.

Substantivity

The attraction between a substrate and a dye or other substance under the precise condition of test whereby the test is selectively extracted from the application medium of substrate. It is the qualitative expression of affinity. Substantivity depends on temperature, type of fiber, electrolyte concentration. Substantive dyes have affinity and are soluble.

Reproducibility of Shades

The shade of the dyes should be reproducible when required. Certain dyes have ability to overcome the factors like liquor ratio, pH, temperature etc. which affect the reproducibility. Characteristics of highly reproducible dyes are:

- Highly soluble
- Medium substantivity
- Medium reactivity
- Good wash off properties
- Highly diffusible

Optimization of Dye

The principle is to carry out dyeing in a manner in which the dyestuffs absorbed by substrate almost uniformly with less dye wastage.

1.Substrate
- Affinity
- Circulation speed
- Action of chemicals before

2.Dyestuff
- Depth of shade
- Optimum quantity/yield
- Diffusion ability and regularity

- Color fastness
- Combination & mixability
- Chromphore percentage

3.Auxiliary Products

- Optimum quantity
- Compatibility with dyestuff and with each other
- Levelness
- Control of PH in final exhaustion
- Reproducibility
- No adverse effect

4. Temperature and time

- Low initial temperature to avoid rapid absorption of dye
- Control of critical temperature zone for maximum exhaustion
- Sufficient time for penetration and fixing

5. Machine

- Control of batch
- Volume of flow
- Temperature regulation

The actual dyeing theory can be obtained mathematically from kinetics of dyeing or dyeing equilibria. The dyeing phenomena found in principle of dyeing curve. The factors for uniform color & optimization of dye all are related to kinetic phenomena. Therefore kinetic dyeing is important in the dyeing process.

Functional Groups of fiber

Cotton: OH-, at higher pH it is ionizable

Wool: -COOH, -NH, -CONH2. At pH 3-4 ionized positively so acid dye is used to dyeing

Acrylic: -COOH, -SO3H, -O SO3H

Silk: -NH2, -CONH

Viscose: -OH, -COOH

Polyester: -OH, -COOH. No ionization effect, high temperature used for dyeing with dispersing.

Diacetate: -OH, -COOCH3

Triacetate: -COOCH3

Dyeing Medium

1. Aqueous medium
   - Water
   - Solvent
   - Foam
2. Vapor phase: cationic, anionic, nonionic

Dyeing Mechanism

The sequence of dyeing falls into four stages

1. Transfer of dye onto fiber surface
2. Adsorption
3. Diffusion into the fiber
4. Interaction

Transfer of dye onto fiber surface

The transfer of dye onto the fiber surface depends on:

1. Environment of the dye bath: environment of the bath refers to
   - Solvent and its type, nature, quantity: solvent may be water and or any other solvents which may be soft/hard, acidic, alkaline, ionic, nonionic etc.
   - pH
   - Dyeing assistants like electrolytes, leveling agents, carrier, dispersing agents etc.
   - temperature of the dyebath which depends on material type (cotton or polyester), type of dye (hot brand or cold brand), method of dyeing (padding or exhaust) Suitable environment ensures easy transference of dye on fiber surface.

2. Substantivity

3. Mechanical and physical force

Adsorption

The distribution process is called adsorption, if the substance which is to be distributed is retained by a surface. The assembly of dye molecules at the fiber surface is governed by: Electropotential forces: All fiber when immersed into water or aqueous solution acquires an electric potential known as ‘zeta potential.’ Cellulosic fiber bears a negative charge while protein fibers at higher pH than its isoelectric point bears are negatively charged and at lower pH than isoelectric point is positively charged. Temperature: most dyes in solution are either in molecular and partially ionized state or exist in the form of ionic micelles; increase in temperature tends to breakdown micelles into less aggregated units. Increase of temperature promotes vibrational activity accelerates the migration of the surface of the fiber.

Agitation: when a fiber is immersed in the dye a large no of molecules tend to enter the fabric at once, thus creating a layer called 'Barrier.' If the dye molecules are to reach the fiber surface then the barrier should be broken which is done by agitation.
Dye adsorption has affect on fastness properties.

Applications

Direct dyes dye all cellulosic fibers, including viscose rayon, and most of them also dye wool and silk. They do not dye acetate rayon and synthetic fibers. Direct dyes can be applied well at low temperatures and are therefore suitable for tie-dyeing and batik work. Generally these dyes are used where high wash fastness is not required

Acid dyes

Highly water soluble, they have good light fastness. The textile acid dyes are suitable for protein fibers: silk, wool, nylon. They contain sodium salt of sulphonic acid so that acid dyes are water soluble. In water and acetic acid, the -NH2 functionalities of the fibres are protonated to give a positive charge: -NH3+., so that there's an interaction with the negative dye charge, allowing the formation of ionic interactions. Also, Van-der-Waals bonds, dipolar bonds and hydrogen bonds are formed between dye and fibre.

Acid dyes Chemical structure

Acid dyes are really complex in structure having also large aromatic molecules, sulphonyl group and amino group to enhance solubility. Acid dyes can be part of the following three main groups: anthraquinone acid dyes, diazo acid dyes, tiphenylmethane acid dyes.

Different kind of acid dyes

Acid dyes can be classified into three classes depending on the leveling properties, economy of the dyeing and fastness properties:

- **Neutral acid dyes:**
  Supra milling or fast acid dyes: they have medium to good wet fastness properties , some of them have low light fastness in pale shades . Usually, these acid dyes are used as self shades only. These are applied to the fiber in a weakly acid pH.
- **Weak acid dyes**
  These dyes belongs to the milling class of dyes. These acid dyes have good fastness properties; light fastness is moderate.
- **Strong acid dyes**
  Acid dyes applied in a strongly acidic medium and called also leveling dyes, wet fastness properties limited. These acid dyes are suitable to produce the combination shades. (e.g. yellow, red, blue).

Classification of acid dyes according to dyeing characteristics

According to their dyeing behavior, especially in relation to the dyeing pH, their migration ability during dyeing and their washing fastness, acid dyes fall into different groups. Acid dyes molecular weight and their degree of sulphonation determine these dyeing features..

The first classification of acid dyes, based on their behaviour in wool dyeing, is the following:

- Level dyeing or equalising acid dyes;
- Fast acid dyes;
- Milling acid dyes;
- Super-milling acid dyes.

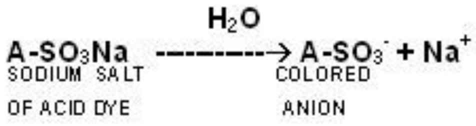
Properties of acid dye

Acid dyes properties:

- acid dyes are anionic in nature.
- acid dyes are suitable for wool, silk, polyamide and modified acrylics.
- Acid dyes are applied from a strongly acidic to neutral pH bath.
- acid dyes only sometimes have affinity for cotton cellulose's , so generally they are not suitable for cellulosic fibers.
- acid dyes link to the fiber by hydrogen bonds , van der waals forces or through ionic interactions.

Mechanism of dyeing

Dissolution of dyes in aqueous solvent, produces a colored anion,



$$\text{A-SO}_3\text{Na} \xrightarrow{H_2O} \text{A-SO}_3^- + \text{Na}^+$$

The protein and polyamide fibers produce cationic sites in water under acidic conditions, as the acidity of the solution is increased more cationic sites are produced under these strongly acidic conditions. These cationic sites are thus available for the acid dye anions to combine with through hydrogen bonding, vander waals forces or ionic bonding. These linkages are strong enough to break, and thus dyeing produced is fast.

POSSIBLE QUESTIONS

PART – B (5 X 8 = 40 MARKS)

1. Discuss the structure and properties of Direct cotton dyes
2. Explain the mechanism of dyeing
3. Discuss the types and properties of acid and basic dyes
4. Explain the affinity of dyes on cellulose and protein fibers
5. Discuss the structure and mechanism of dyeing on substantive dyes
6. Write a note on acid and basic dyes
7. Discuss the difference between acid and basic dyes
8. Describe the major types of direct dyes and its properties
9. Discuss the mechanism of dyeing in detail
10. Explain the chemical reactions involved in the dyeing of cellulose with acid dyes

Unit -2					
……………. group was the first of the synthetic dyes to be taken out of coal-tar derivatives	Cationic Dyes	Anionic dyes	Both A and B	None	**Cationic Dyes**
……………. were originally used to color wool, silk, linen, hemp, etc., without the use of a mordant, or using agent	Basic Dyes	Acid dyes	vat dye	Azoic Dyes	**Basic dyes**
Basic dyes give brilliant colors with exceptional fastness to …………………	acrylic fibers	azoic fibres	Both A and B	None	**acrylic fibers**
Nowadays basic dyes are no longer used to any great extent on …………….	nylon	Cotton	wool	wood	**cotton**
dyes usually have azo linkage……. and high molecular weight	C=C	–N=N-	Both A and B	None	**–N=N-**
………….a very large and important group of dyestuffs	Chrome Dyes	Acid dyes	vat dye	Azoic Dyes	**Acid Dyes**
The first acid dyes were combinations of basic dyes with……	sulphuric or nitric acid	nitric acid or acetic acid	sulphuric or nitric acid	nitric acid or Hydrochloric acid	**sulphuric or nitric acid**
…… cannot be used for wool tops	Mordant dyes	Acid dyes	vat dye	sulfar dyes	**Acid dyes**
A great deal of acid dye is used on ………….	wool carpeting	nylon carpeting	Both A and B	None	**nylon carpeting**
……….is an important group of acid dyes	sulphur dyes	Azoic Dyes	Premetalized Dyes	Disperse dyes	**Premetalized Dyes**
The ………provide very deep shades	Disperse dyes	Acid dyes	sulphur dyes	Azoic Dyes	**sulphur dyes**
sulphur dyes especially the black colors is that they make the….. tender	fabric	Non - fabric	Both A and B	None	**fabric**
Sulphur dyed fabrics therefore usually must be treated with ….. to neutralize the acids, which have formed	alkalis	non alkalis	Both A and B	None	**alkalis**
printing	Mordant dyes	Acid dyes	vat dye	Azoic Dyes	**Azoic Dyes**
Azoic dyes, called ……. in the industry	Naphthols	Anthracene	Both A and B	None	**Naphthols**
The term vat comes from the………. method dyeing in a vat	New Indigo	old indigo	Both A and B	None	**old indigo**
…….. are made from indigo, anthraquinone and carbazole.	Chrome Dyes	Acid dyes	vat dye	Azoic Dyes	**Vat dyes**
…………are insoluble and made soluble by the help of caustic soda and sodium sulfide	Mordant dyes	Sulfar Dyes	vat dye	Azoic Dyes	**Sulfar Dyes**
………… are no water-soluble preparations for dyes.	Soluble Vats	Naphthols	Anthracene	none	**Soluble Vats**
A dispersed dye may be any one of a number of slightly……….. dispersed	soluble dyestuffs	insoluble dyestuffs	Both A and B	None	**soluble dyestuffs**
the dye substance is derived from ………….and azoic dyes	Anthraquinone	Anthraquinone - 2 - sulphonicacid	2-Hydroxyanthraquinone	1-Nitroanthraquinone	**anthraquinone**
……………. are vegetables dyes, originally derived from the madder plant and now produced synthetically	Alizarin Dyes	Acid dyes	vat dye	Azoic Dyes	**Alizarin Dyes**
………….. are produced from the chemical aniline	Pthacyanibe	Aniline Black	Both A and B	None	**Aniline Black**
………. are a special type of acid dyes	Chrome Dyes	Acid dyes	vat dye	Azoic Dyes	**Chrome Dyes**
………… are metal containing acid dyes	Mordant dyes	Neutral Dyes	vat dye	Azoic Dyes	**Neutral Dyes**
………… were originally developed for dyeing secondary cellulose acetate fibers	Disperse dyes	Acid dyes	vat dye	Azoic Dyes	**Disperse dyes**
…………………dyes are relatively insoluble in water	Mordant dyes	Disperse dyes	vat dye	Azoic Dyes	**Disperse Dyes**
Natural dyes can be sorted into ……… categories	one	two	three	four	**three**
Natural dye obtained form plants is ………..	madder	crimson	vermilion	none	**madder**
………… is a dye obtained from an impure earthy ore of iron	clay	sand	Ocher	Mud	**Ocher**
……….. is a constituent of a number of abrasives and pigments.	Hematite	Minerals	ores	pigments	**hematite**
…….. is from the pulpy part of the seeds of Indian plant	Varnishes	ANNATO	Fabric	non fabric	**ANNATO**
A ….. is an element, which aids the chemical reaction that takes place between the dye and the fiber so that the dye is absorbed	mordant	Acid dyes	vat dye	sulfar dyes	**mordant**
Not all dyes need ……	mordants	non mordant	Both A and B	None	**mordants**
Common mordants are………., usually used with cream of tartar	Dye	alum	salt	solid	**alum**
………., which is a brilliant red dye produced from insects living on cactus plants	cochineal	crimson	scarlet dye	None	**cochineal**
……. is extracted from bodies of tiny insect, Coccus arborum	KERMES	Dye	Oak	none	**KERMES**
….. comes from a Central American tree	Azomethane	Anthaquione	logwood	Alizarin	**LOG WOOD**
………… comes chiefly from then inner bark of the black oak	QUERCITRON	Black oak	Red oak	oak	**QUERCITRON**

42 ….. is a chemical that is a by-product of burning coal	Amide	Aniline	phenol	toluene	**Aniline**
The synthetic dyes do not contain the ……….	chemical aniline	chemical Phenol	chemical amide	chemical ester	**chemical aniline**
. Most of the colors can be found in either ,…… or alcohol based dyes.	Vapour based	Alcohal based	water based	oil based	**water based**
Water based dyes can only be applied to unfinished and …….	unsealed wood	sealed wood	Red wood	Sandel wood	**unsealed wood**
…….based dyes if wiped on are as easily applied as the water based	toluene	Alcohol	Amide	Aniline	**Alcohol**
………. is widely used in chocolates	Vanillin	cocoo	Both A and B	None	**Vanillin**
…. preservatives are used primarily to prevent fats from becoming rancid	Antioxidant	Anti bacterial	Antifungal	None	**Antioxidant**
Most preservatives are not believed to a …….	health hazard	Accidents	Wound	Allergy	**health hazard**
In normal temperature alcohol will evaporate slowly enough to allow you…….application time	adequate	in adequate	Both A and B	None	**adequate**
The…… based dyes are reputed to be more color fast than the alcohol reduced dyes	oil	water	acid	crude	**water**
The dyes may show slight differences in color depending on the ……	reducer	oxidizer	Both A and B	None	**reducer**
…… was a coal tar product	synthetic dye	Natural dyes	Both A and B	None	**synthetic dye**
…… comes from the lichen	orchil	litmus	cudbear	colouring	**cudbear**
The leaves were Fermented, the sediment purified, and the remaining substance was pressed into…….	cakes	choclates	Both A and B	None	**cakes**
Dye was supplanted by indigo an ancient shrub well known to the…….	Europeans and Africans	Egyptians and Indians	Both A and B	None	**Egyptians and Indians**
……. used wood to create a blue fabric dye	Europeans	Africans	Asians	None	**Europeans**
………. are used for coloring papers, controlling tint and shade and correction of two sided paper color	Anionic Direct Dyes	Cationic Direct Dyes	Both A and B	None	**Anionic Direct Dyes**
……………. are highly water soluble, they have good light fastness.	Acid dyes	Basic dyes	Disperse dyes	vat dyes	**Acid dyes**
………… are insoluble and made soluble by the help of caustic soda and sodium sulfide	Sulfur Dyes	Acid dyes	Basic dyes	Disperse dyes	**Sulfur Dyes**
……………… are thus available for the acid dye anions to combine with through hydrogen bonding, vander waals forces or ionic bonding.	cationic sites	Anionic sites	Both A and B	None	**cationic sites**

UNIT - III

SYLLABUS

Mordant, Azo and Vat Dyes - Mordant dyes – classification, methods of application; Metal complex dyes – types of bond formation between dye and various fibres.

Azo dyes – Azoic coupling components, protective colloids, electrolytes, stabilisation of diazonium salts, principles and application.

Vat dyes and solubilised vat dyes – classification, methods of application, principles and application, Stripping agents and correction of faulty dyeing.

Mordant Dyes

- The dyes which have no affinity towards textile fibres and are attached with the fibre with the help of mordants are known as mordant dyes.
- Mordant dyes may be organic or inorganic substances. The most commonly used mordant is inorganic chromium. So sometimes these dyes are called chrome dyes.
- These dye molecules have some mordant attracting groups which have some influence on secondary valence bonds due to a particular configuration with metal ions so that insoluble color takes are produced. Mainly neighboring –OH groups or –COOH groups appear in neighboring position in azo dyes. A metal equivalent takes the place of hydrogen in the –OH group or -COOH group each time.
- The mordants have affinity both for fibre and dye. So those dyes which do not have any affinity to fibres can be applied by using a suitable mordant (as dyes have mordant attracting groups)

Properties of Mordant dyes

1. Mordant dyes have no affinity for textile fibres.
2. They are attached to the fibres with the help of mordants. these mordant have affinity both for the dye and fibre.

3. Mordant dyes are capable of combining with metallic oxides to form insoluble color lakes.
4. Mordant dyes may be natural or synthetic.
5. Mordant dyes are mostly applied on natural protein fibres, nylon and acrylic fibres.
6. Good light fastness rating about 4-5
7. Most mordant dye are soluble in cold water.
8. The main feature of the molecule is that, there remains a metal ion as a central atom which is bonded to neighbouring –OH, -COOH or azo group.
9. Wide range of hues can be produced from mordant dyes. The no good blue, green and violet are available for wool. Largely used for black shades.

Classification of Mordant Dyes

On the basis of origin, there are 2 types of mordant dyes:

1. Natural mordant dyes
2. Synthetic mordant dyes

Now they are described below:

1) Natural Mordant Dyes:

Very few natural dyes are color fast with fibres. So mordants are used to fix a dye with the fibre. These dyes as derived from natural source e.g. plants, are natural mordant dyes.

Among the naturally occurring dyes alizarin(1,2-dihydroxy anthraquinine) is extracted from the roots of madder. Alizarin produces red, pink, brown and yellowish brown color when treated with compounds of Al, Sn, Fe and Cu respectively.

Dyeing with natural mordant dyes is a time consuming process. So they are used in lesser extent. In all these dyes chromium or other metals combine chemically with certain groups present in dye and further bounded by other force.

2) Synthetic Mordant Dyes:

As all synthetic mordant dyes are obtained from acid dyes, they are called acid chrome dyes. That is to say,

$$\text{Acid color + Cr} \longrightarrow \text{Acid chrome}$$

These dyes can co-ordinate easily with chromium. They can be dyed as acid dyes and mordanted by after treatment with $K_2Cr_2O_7$ or $Na_2Cr_2O_7$.

These acid chrome dyes are extensively used for wool and polyamide fibres dyeing. They have good wet fastness and most of them possess satisfactory light fastness.

The commonest method of application is to dye in an acid dye bath and when exhaustion is complete, add appropriate amount of dichromate to the liquor. Then boil it for 30 minutes

Example of some synthetic mordant dyes are as below:

Dye	C.I> Number
Chrome Fast Orange R	**Mordant Orange 10**
Solochrome Red B	**Mordant Red 9**
Eriochrome Black T	**Mordant Black 11**

Method of application of Mordant dyes

There are three general method of application of mordant dyes as mentioned below:

1. Chrome mordant process
2. After-chrome mordant process
3. Meta chrome or chromate mordant process

Now they are shortly described below:

1) Chrome mordant process:

This is a two bath process. In this process at first material is impregnated with an insoluble chromium hydrate and then dyeing is done a separate bath.

2) After-chrome mordant process:

This is the oldest and the most common mordant dyeing process. Here the material is first dyed with an acid dye and then mordanting with chromium is carried out in a separate bath. Or mordanting can be done in the same bath after exhaustion of the dye has been completed.

3) Meta chrome/chromate mordant process:

In meta chrome process, dyeing and mordanting are carried out simultaneously in the same bath. Here the mordant is present in the form of chromate which does not form the lake with the dye and which is generally converted into dichromate. The pH of the bath is kept around 6-7.This method has the advantage of facilitating shading and requires less time, then the after-chrome process. It gives highly level of residual chromium in the effluent. This method is now almost obsolete

Metal-complex Dyes

Metal-complex dyes that are otherwise known as pre-metallized dyes shows great affinity towards protein fibers. Generally it has been seen that metal complex dyes are Chromium or Cobalt complexes. Among the popular metal-complex dyes, a variety known as 1:2 metal-complex dyes finds application for dyeing polyamide fibers. For dyeing wool, metal complex dyes are the most favoured. The following table shows a comparison between 1:1 metal-complex and 1:2 metal complex dye.

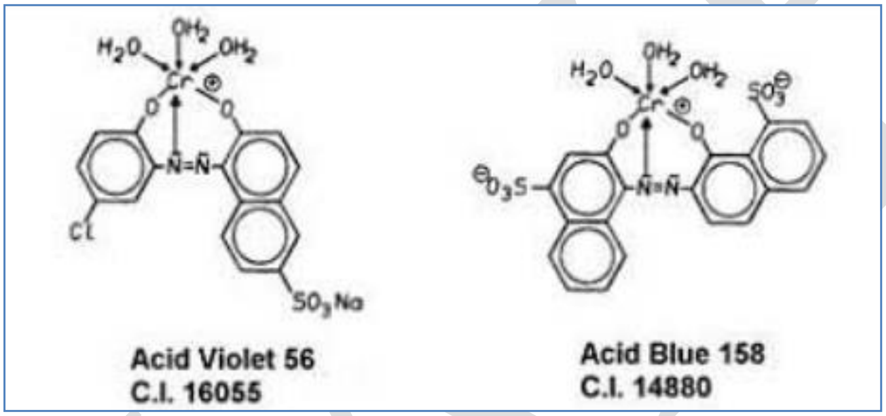
Dye Type	Levelling Ability	Wash Fastness	pH Range
1:1 metal-complex	Good	Good	2
1:2 metal complex	Poor	Very Good	6-7

Metal-complex dyes generally cannot be said as belonging to a particular application dye class. In fact, Metal-complex dyes belong to numerous application classes of dyes. For example, they are found among direct, acid, and reactive dyes. When applied in the dyeing processes, metal-complex dyes are used in pH conditions that is regulated by user class and the type of fiber type (wool, polyamide, etc). The pH levels for wool typically ranges from:

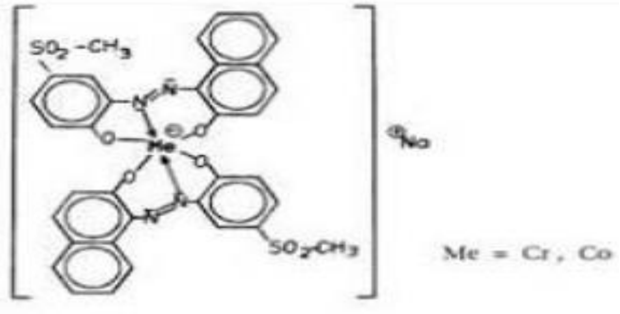
- Strongly acidic (ranging from 1.8 - 4 for 1:1 metal-complex dyes)
- Moderately acidic neutral (ranging from 4 - 7 for 1:2 metal-complex dyes)

Types of Metal Complex Dyes

Chemically speaking, Metalcopmplex Dyes can be broadly classified into two classes. 1:1 metal-complexes, where, one dye molecule gets co-ordinated with a single metal atom. In 1:2 metal complexes, one metal atom is co-ordinated with double dye molecules. The dye molecules are typically a monoazo structure which can contain additional groups like hydroxyl, carboxyl or amino groups. They can form strong co-ordination complexes with transition metal ions, like Nickel, Chromium, Cobalt and Copper. One point to note here is that phthalocyanine dyes are not classified as metal-complex dyes.



Typical molecular structures of 1.1 metal-complex dyes



Typical molecular structures of 1.2 metal-complex dyes

Features of Metal Complex Dyes

- Excellent, light-fastness.
- Medium washing fastness.

- Shows very good level dyeing and penetration characteristics.
- Can cover up for the irregularities in the substrates.

Application of Metal Complex Dyes

Metal Complex Dyes is using for a variety of applications like wood stains, leather finishing, stationery printing inks, inks, coloring for metals, plastic etc.

Types of bond formation between dye and various fibres.

Chemicals Bonds:

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electromagnetic force attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. The reaction between dyes and fibres must take into account the various types of forces exerted by one molecule upon another. All **dyeing** mechanisms can be divided into following three groups:

1. Specific bond between dye and fibre owing to covalent bond, hydrogen bonds or other directed bonds.
2. Non- specific attraction between dye and fibre owing to ion-exchange or Van der Waals' forces.
3. Absence of any interaction, dyes is only mechanically retained. This may be due to insolubilisation of the dye inside the fibre or may be due to self –association into possibly quite large molecular aggregates following their entry into fibre. Aggregation is promoted by a high ratio of molecular weight to ionic group as well as by increase in length of the aromatic structure of the molecule, also by rise in concentration and the presence of inorganic salts, e.g. common salt.

Vander Waal's Forces:

These forces are so named because they were first recognized by Van der Waals in 1873. Very weak forces of attraction are always present between the electrons of one atom and the nucleus of another in close enough proximity. Individually these atoms are very weak forces, but collectively they are considered to be of sufficient strength to be the most important attractive forces between dye and fibre. These forces of attraction are known as Van der Waals' forces. Disperse dyes are held in a polyester fibre by means of Van der Waals' forces.

Hydrogen Bonds:

These forces of attraction are weak forces set up between certain atoms in the dyestuff molecule when they are close enough to other atoms in the fibre. One of these atoms is the hydrogen atom, hence the term "hydrogen bond". Some of the direct and vat dyes are "hydrogen bonded" in the cellulose fibres.

Salt Linkages or Ionic Bond:

These bonds play an important part in dyeing fibre containing amino groups, i.e. wool, silk and nylon with anionic dyes. In the presence of water or dilute acids the amino groups become protonated:

$NH_2CH_2COOH \rightarrow NH_3^+CH_2COO^-$

Acid dyes, being anionic in solution, are attracted at the positive site of the fibre. As the fibre forms zwitterions on ionization, a negative charge is also created on the fibre. This negative charge is responsible for attraction towards basic dyes which forms cationic dye ions in solution. However, basic dyes are now mostly applied on acrylic fibres which contain strong acidic sites. Due to ionization in acidic medium, negative charged sites are created in fibre which attracts **cationic dye** ions.

Ion-Dipole Forces:

While attracting those of opposite charge, ions in solution can exert attraction upon any polar molecule, giving rise to so-called ion-dipole forces. These forces are largely responsible for aqueous solubility of dyes. The attraction between dipoles on the cellulose ether groups and ionic groups in the dye molecules is also proposed.

Covalent Bond

Bonds resulting in very strong chemical forces that are not easy to break expect under serve conditions are called covalent bonds. The classic example is that of the combination of cellulose fibres with reactive dyestuffs, where the hydroxyl group in the cellulose is covalently bonded to a suitable atom in the reactive dye.

Comparison of the Relative Strength of Dye-Fiber Bonds:

Bonds type	Relative strength
Van der Waals' force	1.0
Hydrogen bond	3.0
Ionic bond	7.0
Covalent bond	30.0

Table of Fibers, Dyes and Dye-Fiber Bonds:

Fibre	Dye class having affinity	Types of dye-fibre bonds
Cellulosic: cotton, jute, rayon, etc.	Direct, vat, solublised vat and sulphur dye	Van der Waals' forces and hydrogen bonding
	Reactive dye	Covalent bonds
Protein/polyamide: wool, silk, nylons	Direct, acid,metal complex and basic dye	Ionic bond or electrostatic bonds
	Reactive dye	Covalent bonds
Polyester	Disperse dye	Van der Waals' forces and hydrogen bonding
Acrylic	Cationic	Ionic bond or electrostatic bonds
	Disperse dye	Van der Waals' forces and hydrogen bonding

POSSIBLE QUESTIONS

PART – B (5 X 8 = 40 MARKS)

1. Write a note on Azo dyes
2. Explain the bond formation of dyes with various fibers
3. Give a detail account on vat dyes
4. Explain in detail about the mordant dyes
5. Explain in detail about the azoic coupling components
6. Discuss the vat dyes and solubilised vat dyes
7. Explain in detail about the azo dyes and vat solublised dyes
8. Describe the synthesis, properties and applications of mordant dyes
9. What are the difference between vat dyes and mordant dyes?
10. What is the effect of electrolytes and protective colloids on dyeing?

UNIT 3

Questions	A	B	C	D	ANSWER
Unit-3					
The dyes which have no affinity towards textile fibres and are attached with the fibre with the help of mordants are known ………………	Mordant dyes	Azo dyes	vat dye	sulfar dyes	**Mordant dyes**
…………….. may be organic or inorganic substances.	Mordant dyes	Azo dyes	vat dye	sulfar dyes	**Mordant dyes**
The most commonly used mordant is …………….	inorganic chromium	inorganic sulfar	Both A and B	None	**inorganic chromium**
Mainly neighbouring ……………………… appear in neighbouring position in azo dyes.	SH groups	OH groups	NH groups	None	**–OH groups or –COOH groups**
The mordants have affinity both for ………..	fibre and dye	nylon and wool	cotton and wool	cotton and silk	**fibre and dye**
Mordant dyes have no affinity for …….. fibres.	textile	nylon	wool	scouring	**textile**
Mordant dyes are capable of combining with ………. to form insoluble color lakes.	non metallic oxides	metallic oxides	Both A and B	None	**metallic oxides**
Mordant dyes may be …………	natural or synthetic	only natural	only synthetic	none	**natural or synthetic**
Mordant dyes are mostly applied on natural protein fibres, nylon and …………….	azoic fibres	acrylic fibres	Both A and B	None	**acrylic fibres**
Mordant dyes are Good light fastness rating about ……….	4,5	3,6	2,2	1,1	**4,5**
Most mordant dye are soluble in ……..water	Cold	Hot	Both A and B	None	**cold**
Wide range of …….. can be produced from mordant dyes	hues	non hues	Both A and B	None	**hues**
There are ……… types of mordant dyes	one	two	three	four	**two**
Very few natural dyes are color fast with………	protein	Protopectinases	Vitamin	Fibre	**fibres**
Mordants are used to fix a dye with the …….	protein	Protopectinases	Vitamin	Fibre	**fibre**
Among the naturally occurring dyes ………. is extracted from the roots of madder	Alizarin	logwood	Azomethane	Anthaquione	**alizarin**
…………….. produces red, pink, brown and yellowish brown color when treated with compounds of Al, Sn, Fe and Cu respectively.	Alizarin	logwood	Azomethane	Anthaquione	**Alizarin**
……….. with natural mordant dyes is a time consuming process	Dyeing	pigments	complex	colours	**Dyeing**
synthetic mordant dyes are obtain from acid dyes, they are called…………….	acid chrome dyes.	Base Chrome dyes	Both A and B	None	**acid chrome dyes.**
………. are extensively used for wool and polyamide fibres dyeing	Base Chrome dyes	acid chrome dyes.	Both A and B	None	**acid chrome dyes**
……….is impregnated with an insoluble chromium hydrate and then dyeing is done a separate bath.	Chrome mordant process	After Chrome mordant process	Both A and B	None	**Chrome mordant process**
……….oldest and the most common mordant dyeing process.	Chrome mordant process	After Chrome mordant process	Both A and B	None	**After-chrome mordant process**
In meta chrome process, dyeing and mordanting are carried out simultaneously in the ……….	same bath	different bath	Both A and B	None	**same bath**
The pH of the bath is kept around……. in met chrome process	6-7	2-4	9-11	above 12	**6-7**
…….. method is now almost obsolete	meta chrome process	Base Chrome dyes	acid chrome dyes.	para chrome process	**meta chrome process**
Metal-complex dyes that are otherwise known as …….	pre-metallized	post metallized	Both A and B	None	**pre-metallized**
Metal complex dyes are ……………. complexes	Chromium or Cobalt	Chromium or Magnesium	Cobalt and Magnesium	None	**Chromium or Cobalt**
A variety known as ………….dyes finds application for dyeing polyamide fibers	1:2 metal-complex	2:2 metal-complex	3:2 metal-complex	2:1 metal-complex	**1:2 metal-complex**
For dyeing wool, ……….. dyes are the most favoured	Metal complex dyes	Sulfar dyes	Direct dye	acid dye	**metal complex**
Metal-complex dyes generally cannot be said as belonging to a particular application dye class	Metal complex dyes	Sulfar dyes	Direct dye	acid dye	**Metal-complex**
Moderately acidic neutral, ranging from ……. for 1:2 metal-complex dyes.	4 to 7	6 to 8	7 to 4	8 to 6	**4 to 7**
In 1:2 metal complexes, one metal atom is co-ordinated with ……. molecules	Mordant dyes	Azo dyes	double dye	sulfar dyes	**double dye**
……….. dyes are not classified as metal-complex dyes.	Methyl orange	phthalocyanine	Both A and B	None	**phthalocyanine**

……………… are excellent light fast ness	Metal Complex Dyes	Azo dyes	Acid dye	sulfar dyes	**Metal Complex Dyes**
Metal Complex Dyes is using for a variety of applications like ……………	wood stains	plastic	Both A and B	None	**wood stains**
All dyeing mechanisms can be divided into …….groups	one	two	three	four	**three**
Specific bond between dye and fibre owing to ………………, hydrogen bonds or other directed bonds.	Hydrogen bond	covalent bond	ionic bond	none	**covalent bond**
Non- specific attraction between dye and fibre owing to ion-exchange or ………….	Van der Waals' forces	Hydrogen bonding	covalent bonding	ionic bonding	**Van der Waals' forces**
………. are held in a polyester fibre by means of Van der Waals' forces.	Disperse dyes	Azo dyes	Acid dye	sulfar dyes	**Disperse dyes**
Some of the direct and vat dyes are……………… in the cellulose fibres.	hydrogen bonded	covalent bonding	ionic bonding	none	**hydrogen bonded**
Due to ionization in acidic medium, negative charged sites are created in fibre which attracts…….	cationic dye ions	Anionic dye ions	Both A and B	None	**cationic dye ions**
Ion-Dipole Forces are largely responsible for …………of dyes.	**aqueous solubility**	non aqueous	Both A and B	None	**aqueous solubility**
Bonds resulting in very strong chemical forces that are not easy to break expect under serve conditions are called …….	chemical bond	Ionic bond	covalent bond	Coordination bond	**covalent bonds**
The………… in the cellulose is covalently bonded to a suitable atom in the reactive dye.	hydroxyl groups	azo groups	thiol groups	None	**hydroxyl group**
……., being anionic in solution, are attracted at the positive site of the fibre	Mordant dyes	Azo dyes	Acid dye	sulfar dyes	**Acid dyes**
Basic dyes are now mostly applied on …..	acrylic fibres	protein fibres	nylon fibres	none	**acrylic fibres**
………………. play an important part in dyeing fibre containing amino groups	chemical bond	Ionic bond	covalent bond	Coordination bond	**Ionic Bond**
Hydrogen Bonds forces of attraction are weak forces set up between certain atoms in the…….	Pigments	dyestuff molecule	Both A and B	None	**dyestuff molecule**
……………..most important attractive forces between dye and fibre	Van der Waals' forces	Hydrogen bonding	covalent bonding	ionic bonding	**Van der Waals' forces**
,………. of attraction are always present between the electrons of one atom and the nucleus of another in close enough proximity	weak forces	strong force	moderate force	None	**weak forces**
………………...forces are so named because they were first recognized by Van der Waals in 1873	Van der Waals' forces	Hydrogen bonding	covalent bonding	ionic bonding	**Van der Waals' forces**
Absence of any interaction, ….. is only mechanically retained	Dye	Azo dyes	Acid dye	sulfar dyes	**dyes**
………. is promoted by a high ratio of molecular weight to ionic group	Dispersion	Aggregation	Both A and B	None	**Aggregation**
A …….. is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms	chemical bond	Ionic bond	covalent bond	Coordination bond	**chemical bond**
Metal Complex Dyes Shows very good level dyeing and………..	depenetration	penetration	Both A and B	None	**penetration**
The dye molecules are typically a monoazo structure which can contain additional groups like ………	amino groups	thiol	NO_2	Cl	**amino groups**
The ….. is present in the form of chromate which does not form the lake with the dye	Mordant	Azo dyes	Both A and B	None	**mordant**
……….. can be done in the same bath after exhaustion of the dye has been completed.	Azo dyes	Acid dye	Mordanting	sulfar dyes	**Mordanting**
……………… is general method of application of mordant dyes	Non-Chrome mordant process	Chrome mordant process	Both A and B	None	**Chrome mordant process**

UNIT - IV

SYLLABUS

Disperse dyes

Chemistry involved in the production of Aniline black; Prussian black and phthalocyanines. Disperse dyes - classification based on chemical structure, properties and principles of application; Solvent soluble dyes - Nigrosines and Indulines; Cyanine dyes.

Prussian blue

It is a dark blue pigment with the idealized chemical formula Fe7(CN)18. To better understand the binding situation in this complex compound the formula can also be written as $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$. Another name for the color is Berlin blue in painting, Parisian or Paris blue. Turnbull's blue is the same substance, but is made from different reagents, and its slightly different color stems from different impurities.

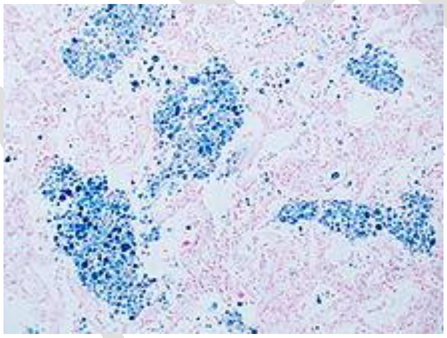
Prussian blue was the first modern synthetic pigment. It is employed as a very fine colloidal dispersion, as the compound itself is not soluble in water. It is famously complex, owing to the presence of variable amounts of other ions and the sensitive dependence of its appearance on the size of the colloidal particles formed when it is made. The pigment is used in paints, and it is the traditional "blue" in blueprints and aizuri-e Japanese woodblock prints.

In medicine, Prussian blue is used as an antidote for certain kinds of heavy metal poisoning, e.g., by thallium and radioactive isotopes of caesium. In particular it was used to absorb 137 Cs+ from those poisoned in the Goiânia accident. Prussian blue is orally administered. The therapy exploits Prussian blue's ion exchange properties and high affinity for certain "soft" metal cations.

It is on the World Health Organization's List of Essential Medicines, the most important medications needed in a basic health system. Prussian blue lent its name to prussic acid (hydrogen cyanide), which was derived from it. In Germany, hydrogen cyanide is called Blausäure ("blue acid"), and Joseph Louis Gay-Lussac gavecyanide its name, from the Greek word κυανός (kyanos, "blue"), because of the color of Prussian blue.

Medicine

Prussian blue's ability to incorporate monocations makes it useful as a sequestering agent for certain heavy metal poisons. Pharmaceutical-grade Prussian blue in particular is used for people who have ingested thallium or radioactive caesium. According to the International Atomic Energy Agency, an adult male can eat at least 10 g of Prussian blue per day without serious harm. The U.S. Food and Drug Administration has determined the "500-mg Prussian blue capsules, when manufactured under the conditions of an approved New Drug Application, can be found safe and effective therapy" in certain poisoning cases. Radiogardase (Prussian blue in soluble capsules) is a commercial product for the removal of caesium-137 from the intestine, so indirectly from the bloodstream by intervening in the enterohepatic circulation of caesium-137, reducing the internal residency time (and exposure) by about two-thirds.



Prussian blue stain

Prussian blue is a common histopathology stain used by pathologists to detect the presence of iron in biopsy specimens, such as in bone marrow samples. The original stain formula, known historically (1867) as "Perls' Prussian blue" after its inventor, German pathologist Max Perls (1843–1881), used separate solutions of potassium ferrocyanide and acid to stain tissue (these are now used combined, just before staining). Iron deposits in tissue then form the purple Prussian blue dye in place, and are visualized as blue or purple deposits. The formula is also known as Perls Prussian blue and (incorrectly) as Perl's Prussian blue.

Engineer's blue, Prussian blue in an oily base, is the traditional material used for spotting metal surfaces such as surface plates and bearings for hand scraping. A thin layer of nondrying paste is applied to a reference surface and transfers to the high spots of the workpiece. The toolmaker then scrapes, stones, or otherwise removes the marked high spots. Prussian blue is preferable because it will not abrade the extremely precise reference surfaces as many ground pigments may.

Analytical chemistry

Prussian blue is formed in the Prussian blue assay for total phenols. Samples and phenolic standards are given acidic ferric chloride and ferricyanide, which is reduced to ferrocyanide by the phenols. The ferric chloride and ferrocyanide react to form Prussian blue. Comparing the absorbance at 700 nm of the samples to the standards allows for the determination of total phenols or polyphenols.

Production

Prussian blue is produced by oxidation of ferrous ferrocyanide salts. These white solids have the formula $M_2Fe[Fe(CN)_6]$ where

$M^+ = Na^+$ or K^+

The iron in this material is all ferrous, hence the absence of deep color associated with the mixed valency. Oxidation of this white solid with hydrogen peroxide or sodium chlorate produces ferricyanide and affords Prussian blue. A "soluble" form, $K[Fe^{III}Fe^{II}(CN)_6]$, which is really colloidal, can be made from potassium ferrocyanide and iron(III):

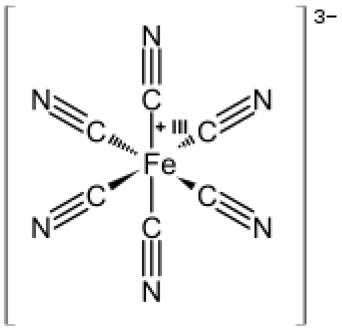
$$K^+ + Fe^{3+} + [Fe^{II}(CN)6]^{4-} \rightarrow K\,Fe^{III}[Fe^{II}(CN)_6]$$

The similar reaction of potassium ferricyanide and iron(II) results in the same colloidal solution, because $[Fe^{III}(CN)^6]^{3-}$ is converted into ferrocyanide. "Insoluble" Prussian blue is produced if, in the reactions above, an excess of Fe^{3+} or Fe^{2+}, respectively, is added.

In the first case:

$$4Fe^{3+} + 3[Fe^{II}(CN)_6]^{4-} \rightarrow Fe^{III}[Fe^{III}Fe^{II}(CN)_6]_3$$

Turnbull's blue



Ferricyanide ion, used to make Turnbull's blue

In former times, the addition of iron (II) salts to a solution of ferricyanide was thought to afford a material different from Prussian blue. The product was traditionally named Turnbull's Blue (TB). It has been shown, however, by means of X-ray diffraction and electron diffraction methods, that the structures of PB and TB are identical. The differences in the colors for TB and PB reflect subtle differences in the method of precipitation, which strongly affects particle size and impurity content.

Properties

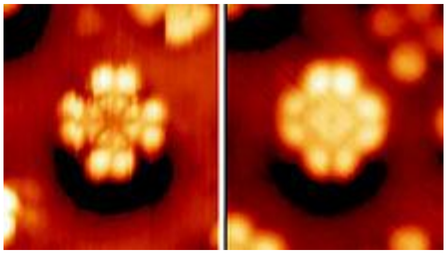
Prussian blue is a microcrystalline blue powder. It is insoluble, but the crystallites tend to form a colloid. Such colloids can pass through fine filters. Despite being one of the oldest known synthetic compounds, the composition of Prussian blue remained uncertain for many years. Its precise identification was complicated by three factors:

1. Prussian blue is extremely insoluble, but also tends to form colloids.
2. Traditional syntheses tend to afford impure compositions.
3. Even pure Prussian blue is structurally complex, defying routine crystallographic analysis.

Phthalocyanine

Phthalocyanine is an organic compound with the formula $(C_8H_4N_2)_4H_2$. It is classified as an aromatic macrocyclic compound. The organic compound is only of theoretical or specialized interest, but its metal complexes are valuable as dyes, pigments, and catalysts.

Properties



STM images of individual phthalocyanine molecules recorded at a bias of −2 V (left) and +1 V (right). Note that STM probes density of electrons in theHOMO/LUMO bands rather than atomic profiles

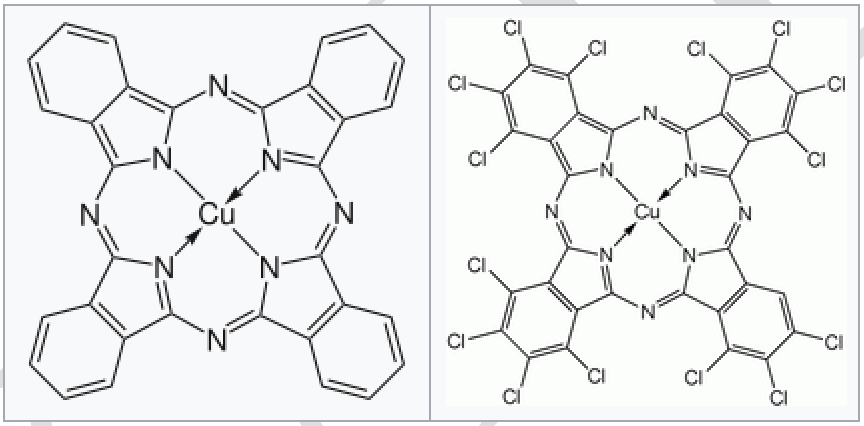
Unsubstituted phthalocyanine, abbreviated H 2Pc, and many of its complexes have very low solubility in organic solvents. Benzene at 40 °C dissolves less than a milligram of H_2Pc or CuPc per litre. H_2Pc or CuPc dissolve easily in sulfuric acid due to the protonation of the nitrogen atoms bridging the pyrrole rings. Many phthalocyanine compounds are thermally very stable, do not melt but can be sublimed, CuPc sublimes at >500 °C under inert gases (nitrogen, CO_2). Substituted phthalocyanine complexes often have much higher solubility. They are less thermally stable and often cannot be sublimed. Unsubstituted phthalocyanines strongly absorb light between 600 and 700 nm, thus these materials are blue or green. Substitution can shift the absorption towards longer wavelengths, changing the color from pure blue to green to colorless (when the absorption is in the near infrared).

Many derivatives of the parent phthalocyanine are known, where either carbon atoms of the macrocycle are exchanged for nitrogen atoms or where the hydrogen atoms of the ring are substituted by functional groups like halogens, hydroxy, amino, alkyl, aryl, thiol, alkoxy, nitro, etc. groups. Structurally larger analogues include naphthalocyanines.

Synthesis

Phthalocyanine forms upon heating various phthalic acid derivatives contain nitrogenous functional groups, e.g. phthalonitrile and diiminoisoindole. Alternatively the presence of urea, the heating of phthalanhydride gives H_2Pc

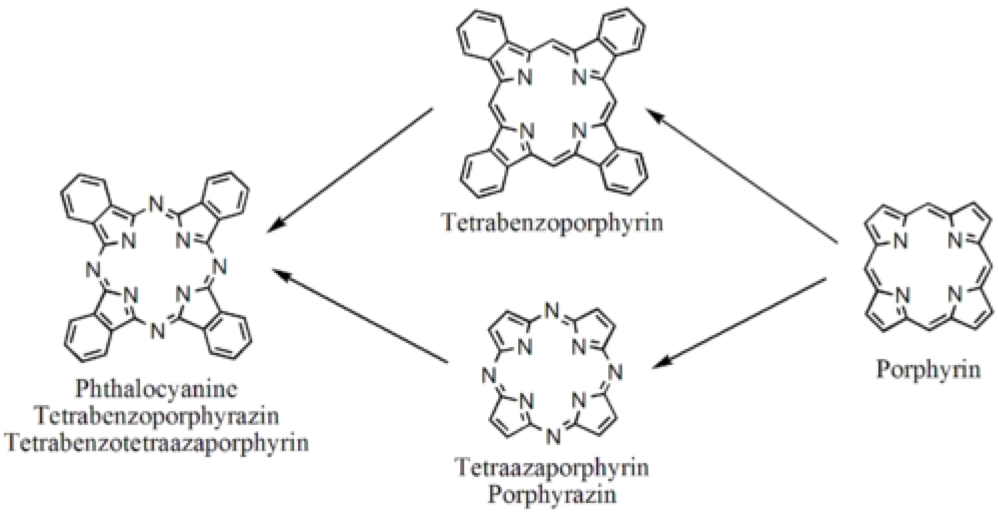
The preparation of H_2Pc is not conducted often, in contrast to the preparation of the metal complexes. Several of these starting materials are shown in the figure. To prepare these complexes, the reactions of the phthalonitriles is conducted in the presence of metal salts. Using such methods, approximately 57000 tonnes of various phthalocyanines were produced in 1985.



Halogenated and sulfonated derivatives of copper phthalocyanines are commercially important. Such compounds are prepared by treating CuPc with chlorine, bromine or oleum.

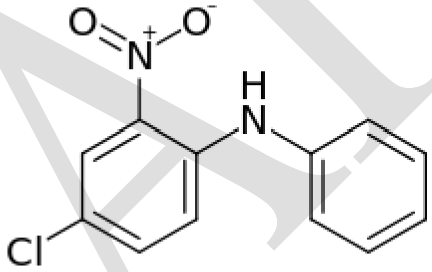
Other examples

Phthalocyanines are closely related to other tetrapyrrole macrocyles including porphyrins and porphyrazines. Phthalocyanines are structurally related to other macrocyclic pigments, especially the porphyrins. Both feature four pyrrole-like subunits linked to form a 16-membered ring. The pyrrole-like rings within H 2Pc are closely related to isoindole. Both porphyrins and phthalocyanines function as planar tetradentate dianionic ligands that bind metals through four inwardly projecting nitrogen centers. Such complexes are formally derivatives of Pc2−, the conjugate base of H2Pc.



Relationship of the phthalocyanine with the porphyrin macrocycle

Disperse dye:



Disperse Yellow 26

Disperse dyes are the only water-insoluble dyes that dye polyester and acetate fibers. Disperse dye molecules are the smallest dye molecules among all dyes.

A disperse dye molecule is based on an azobenzene (as Disperse Red 1 or Disperse Orange 37) or anthraquinone molecule with nitro, amine, hydroxyl, etc. groups attached to it.

Classification of Disperse Dyes

According to Chemical Structure:

According to chemical structure there are following types of disperse dyes:

1. Nitro Dyes
2. Amino Ketone dyes
3. Anthraquinonoid dyes
4. Mono azo dyes
5. Di- azo dyes

According to Fastness Property:

According to fastness properties there are following 4 types of disperse dyes:

1. Group A: These dyes have excellent dyeing properties and good fastness properties.
2. Group B: These dyes are excellent in high temperature and for carrier dyeing with moderate fastness.
3. Group C: These dyes are moderate for carrier and high temperature dyeing with higher fastness property than group B dyes.
4. Group D: These dyes are of excellent fastness to heat but for dyeing properties on carrier method.

According to Energy Requirement:

According to energy required for dyeing there are following 3 types of disperse dyes:

1. Low energy dyes: These dyes are used to dye with carrier. For dyeing 77°C temperature is required. They have extremely poor resistance to sublimation.

2. Medium energy dyes: These dyes are used to dye mostly in between temperature 104°C-110°C which provides better sublimation fastness than that of low energy dyes.
3. High energy dyes: These dyes are used to dye at temperature above 129°C and are suitable for continuous dyeing. They provide all round fastness properties.

Chemical Groups In Disperse Dyes

The percentage of chemical groups present in disperse dyes are as below:

- Mono azo dyes →→→→→→→→ → 50%
- Anthraquinonoid dyes →→→→→→ 25%
- Diazo dyes →→→→→→→→→→→ 10%
- Methyne dyes →→→→→→→→→ 03%
- Styryl dyes →→→→→→→→→→ 03%
- Acrylene benzimidazol →→→→→ 03%
- Quinonaphthalon dyes →→→→→ 03%
- Amino naphthyl amide→→→→→ 01%
- Napthoquinone imine →→→→→ 01%
- Nitro disperse dyes →→→→→→ 01%

Total →→→→→→ 100%

Trade Names Of Disperse Dyes

Name of dye	Manufacturer	Origin
Foron	Sandoz	Switzerland
Terasil	Ciba-Geigy	Switzerland
Dispersol	ICI	UK
Samaron	Hoechst	Germany
SRA	British Celanese Ltd.	UK
Setile	ACNA	Italy

POSSIBLE QUESTIONS

PART – B (5 X 8 = 40 MARKS)

1. Write a note on Solvent soluble dyes
2. Explain the properties and applications of Disperse dyes
3. Write a note on (i) Prussian black (ii) Aniline black
4. Explain the types and properties of cyanine dyes
5. Write a note on (i) Nigrosines (ii) Indulines
6. Explain the chemistry involved in the production of Prussian black
7. Explain the chemistry and applications of Disperse dyes
8. Describe the chemistry involved in phthalocyanines
9. What are the chemistry involved in solvent soluble dyes
10. Describe the classification, properties of disperse dyes

Unit-4					Answers
……………..is a dark blue pigment with the idealized chemical formula $Fe_7(CN)_{18}$	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
Prussian blue was the first modern ………………	Dyes	synthetic pigment	Both A and B	None	synthetic pigment
………… is used as an antidote for certain kinds of heavy metal poisoning,	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
……….. is a microcrystalline blue powder	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
Hydrogen cyanide is called…………	Blue acid	Red acid	orange acid	Black acid	Blue acid
The ……….and ferrocyanide react to form Prussian blue	ferric sulphate	ferric chloride	ferric nitrate	none	ferric chloride
Prussian blue is produced by …….. of ferrous ferrocyanide salts	Oxidation	Reduction	Halogenation	Sulphonation	oxidation
Prussian blue is extremely insoluble, but also tends to form ………..	Colloids	Alkaloids	Both A and B	None	colloids
…………… is an organic compound with the formula $(C_8H_4N_2)_4H_2$	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Phthalocyanine
………….. is classified as an aromatic macrocyclic compound.	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Phthalocyanine
Prussian blue is a microcrystalline ………..powder	Blue acid	Red acid	orange acid	Black acid	blue
……..images of individual phthalocyanine molecules recorded at a bias of −2 V (left) and +1 V(right)	SEM	SVET	STM	AFM	STM
Benzene at 40 °C dissolves less than a ……….. of H2Pc	milligram	microgram	millimole	micromole	milligram
Many phthalocyanine compounds are thermally……	very stable	less stable	moderately stable	None	very stable
Phthalocyanine forms upon heating various phthalic acid derivatives contain……………. functional groups	Nitrogen	Sulphur	Chlorine	Bromine	nitrogen
The presence of urea, the heating of phthalanhydride gives………	H2Pc	Pt	Pd	V_2O_5	H2Pc
The reactions of the phthalonitriles is conducted in the presence of	Non metal salts	metal salts	Both A and B	None	metal salts
Approximately…………. of various phthalocyanines were produced in 1985.	67000 tonnes	57000 tonnes	85000 tonnes	94000 tonnes	57000 tonnes
Halogenated and …………. derivatives of copper phthalocyanines are commercially important	sulfonated	Aminated	chlorinated	Brominated	sulfonated derivatives

Phthalocyanines are closely related to other tetrapyrrole macrocyles including ……………	porphyrins and porphyrazines	Pyridine and porphyrins	Pyrimidine and porphyrazines	Pyridine and Pyrimidine	porphyrins and porphyrazines
Phthalocyanines are structurally related to other macrocyclic pigments, especially the …………….	porphyrins	porphyrazines	Pyrimidine	Pyridine	porphyrins
……………….. function as planar tetradentate dianionic ligands that bind metals through four inwardly projecting nitrogen centers	porphyrins and phthalocyanines	Pyridine and porphyrins	Pyrimidine and porphyrazines	None	porphyrins and phthalocyanines
……………….. are the only water-insoluble dyes that dye polyester and acetate fibers.	Disperse dyes	Acid dyes	Basic dyes	Vat dyes	Disperse dyes
A disperse dye molecule is based on an ……………	azobenzene	chlorobenzene	thiobenzene	None	azobenzene
……… dyes have excellent dyeing properties and good fastness properties.	Group A	Group B	Group C	Group D	Group A
……………. are used to dye with carrier. For dyeing 77°C temperature is required.	Low energy dyes	High energy dyes	Both A and B	None	Low energy dyes
………… are used to dye at temperature above 129°C and are suitable for continuous dyeing	Low energy dyes	High energy dyes	Both A and B	None	High energy dyes
The percentage of chemical groups present in Mono azo dyes ………	15%	25%	50%	75%	50%
……… is used as an antidote for certain kinds of heavy metal poisoning	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
The therapy exploits Prussian blue's ion exchange properties and high affinity for certain …….. metal cations.	soft	Hard	Both A and B	None	soft
……… lent its name which was derived from prussic acid (hydrogen cyanide)	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
In Germany, hydrogen cyanide is called……….	Blue acid	Red acid	orange acid	Black acid	Blue acid
………. was the first modern synthetic Blausäure	Dyes	Pigments	Both A and B	None	pigment
………… is used as an antidote for certain kinds of heavy metal poisoning	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
……..is preferable because it will not abrade the extremely precise reference surfaces as many ground pigments may	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue

The absorbance at …….. of the samples to the standards allows for the determination of total phenols or polyphenols.	700 nm	500 nm	300 nm	100 nm	700 nm
Substituted phthalocyanine complexes often have much …………	higher solubility	lower solubility	Partially soluble	None	higher solubility
Unsubstituted phthalocyanines strongly absorb light between ……….	400 and 500 nm	500 and 700 nm	600 and 700 nm	700 and 800 nm	600 and 700 nm
Substitution can shift the absorption towards longer wavelengths, changing the color from pure……………. to green to colorless	Blue	Red	Orange	Black	blue
The pyrrole-like rings within H 2Pc are closely related to ……	isoindole	isopyrrole	Both A and B	None	isoindole
…….. molecules are the smallest dye molecules among all dyes.	Disperse dyes	Acid dyes	Basic dyes	Vat dyes	Disperse dye
……….. are moderate for carrier and high temperature dyeing with higher fastness property than group B dyes	Group A	Group B	Group C	Group D	Group C
The percentage of chemical groups present in Methyne dyes …….	1%	2%	3%	4%	3%
The percentage of chemical groups present in Diazo dyes …….	10%	20%	30%	40%	10%
The percentage of chemical groups present in Styryl dyes is ………..	1%	2%	3%	4%	3%
The percentage of chemical groups present in Quinonaphthalon dyes…………	1%	2%	3%	4%	3%
……..is the manufracturer of foron dye	Hoechst	ACNA	Sandoz	ICI	Sandoz
The origin of Hoechst is ………	UK	USA	Australia	Germany	Germany
the origin of SKA dye is ……	UK	USA	Australia	Japan	Uk
The Manufactureof Foron dye is ……………	Hoechst	ACNA	Sandoz	ICI	Sandoz
……..is the manufracturer of Setile dye	Hoechst	ACNA	Sandoz	ICI	ACNA
According to chemical structure there are ………types of disperse dyes	1	3	5	7	5
A disperse dye molecule is based on an	azobenzene	chlorobenzene	thiobenzene	None	azobenzene
porphyrin macrocycle has simillar relationship with ……………………	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Phthalocyanine

Alternatively the presence of……., the heating of phthalanhydride gives H2Pc	Urea	Thiourea	Methl urea	Phenyl urea	urea
……….probes density of electrons in the HOMO/LUMO bands rather than atomic profiles	SEM	SVET	STM	AFM	STM
…………. is preferable because it will not abrade the extremely precise reference surfaces	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
Iron deposits in tissue then form the purple …………. dye in place, and are visualized as blue or purple deposits	Aniline black	Prussian blue	phthalocyanines	Cyanine dyes	Prussian blue
………… is a mixture of synthetic black dyes made by heating a mixture of nitrobenzene, aniline, and hydrochloric acid in the presence of a copper or iron	Nigrosines	Aniline black	Prussian blue	phthalocyanines	Nigrosines
…… is a dye of blue, bluish-red or black shades.	Induline	Nigrosines	Cyanine dyes	Aniline black	Induline

UNIT - V

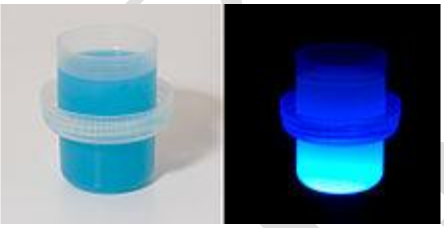
SYLLABUS

Colour and Brightening Agents

Fluorescent brightening agents (FBA) - Theory and applications; Identification and estimation of dyes on fibres; The action of light on dyes and dyed fibres; Mechanism of fading.

Fluorescent brightening agents (FBA):

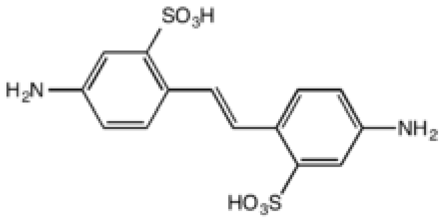
Optical brighteners, optical brightening agents (OBAs), fluorescent brightening agents (FBAs), or fluorescent whitening agents (FWAs), are chemical compounds that absorb light in the ultraviolet and violet region (usually 340-370 nm) of the electromagnetic spectrum, and re-emit light in the blue region (typically 420-470 nm) by fluorescence. Fluorescent emission is a short-lived period of light emission by a fluorophore, unlikephosphorescence, which is long-lived. These additives are often used to enhance the appearance of color of fabric and paper, causing a "whitening" effect; they make intrinsically yellow/orange materials look less so, by compensating the deficit in blue and purple light reflected by the material, with the blue and purple optical emission of the fluorophore.



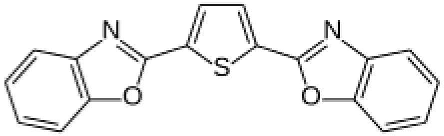
Laundry detergent fluorescing under ultraviolet light

Properties of Fluorescent brightening agents (FBA):

The most common classes of compounds with this property are the stilbenes, e.g., 4,4′-diamino-2,2′-stilbenedisulfonic acid. Older, non-commercial fluorescent chemicals include as umbelliferone, which absorbs in the UVportion of the spectrum and re-emit it in the blue portion of the visible spectrum. A white surface treated with an optical brightener can emit more visible light than that which shines on it, making it appear brighter. The blue light emitted by the brightener compensates for the diminishing blue of the treated material and changes the hue away from yellow or brown and toward white.



4,4′-diamino-2,2′-stilbenedisulfonic acid is a popular optical brightener.



4 4'-bis(benzoxazolyl)-cis-stilbene and 2 5-bis(benzoxazol-2-yl)thiophene (shown here) are also an intensely fluorescent and used as optical brighteners, e.g., in laundry detergents.

Approximately 400 brightener types are listed in the Colour Index, but fewer than 90 are produced commercially, and only a handful is commercially important. Generically, the C.I. FBA number can be assigned to a specific substance; however, some are duplicated, since manufacturers apply for the index number when they produce it. The global OBA production for paper, textiles, and detergents is dominated by just a few di- and tetra-sulfonated triazole-stilbenes and a di-sulfonated stilbene-biphenyl derivatives. The stilbene derivatives are subject to fading upon prolonged exposure to UV, due to the formation of optically inactive cis-stilbenes. They are also degraded by oxygen in air, like most dye colorants. All brighteners have extended conjugation and/or aromaticity, allowing for electron movement. Some non-stilbene brighteners are used in more permanent applications such as whitening synthetic fiber.

Brighteners can be "boosted" by the addition of certain polyols, such as high molecular weight polyethylene glycol or polyvinyl alcohol. These additives increase the visible blue light emissions significantly. Brighteners can also be "quenched". Excess brightener will often cause a greening effect as emissions start to show above the blue region in the visible spectrum.

Application of Fluorescent brightening agents (FBA):

Brighteners are commonly added to laundry detergents to make the clothes appear cleaner. Normally cleaned laundry appears yellowish, which consumers do not like. Optical brighteners have replaced bluing which was formerly used to produce the same effect.

Brighteners are used in many papers, especially high brightness papers, resulting in their strongly fluorescent appearance under UV illumination. Paper brightness is typically measured at 457 nm, well within the fluorescent activity range of brighteners. Paper used for banknotes does not contain optical brighteners, so a common method for detecting counterfeit notes is to check for fluorescence.

Optical brighteners have also found use in cosmetics. One application is to formulas for washing and conditioning grey or blonde hair, where the brightener can not only increase the luminance and sparkle of the hair, but can also correct dull, yellowish discoloration without darkening the hair. Some advanced face and eye powders contain optical brightener microspheres that brighten shadowed or dark areas of the skin, such as "tired eyes".

A side effect of textile optical whitening is to make the treated fabrics more visible with Night Vision Devices than non-treated ones. This may or may not be desirable for military or other applications.[citation needed]Optically brightened paper is often not useful in exacting photographic or art applications, since the whiteness decreases with time.

End uses of optical brighteners include:

1. Detergent whitener (instead of bluing agents)
2. Paper brightening (internal or in a coating)
3. Fiber whitening (internal, added to polymer melts)
4. Textile whitening (external, added to fabric finishes)
5. Color-correcting or brightening additive in advanced cosmetic formulas (shampoos, conditioners, eye makeup)

The action of light on dyes:

Dyes and pigments work by absorbing certain wavelengths of light and reflecting or transmitting the rest. When a dye molecule absorbs a photon, an electron is excited to a higher energy state. Most of the time (neglecting fluorescence), the molecule de-excites by giving off heat and returns to the ground state intact. However, because the excited state is a high energy state, it has the potential to undergo a chemical reaction, breaking a covalent bond or otherwise irreversibly reacting with another molecule. This changes the electronic structure of the molecule which changes its absorption properties: e.g. many dyes that absorb visible light have large systems of conjugated double bonds and if these are broken, the absorbance can shift to much shorter wavelengths. How likely this kind of destructive chemistry is depends on the nature of the dye. Organic dyes tend to be more susceptible to photo bleaching than things like quantum dots and inorganic pigments.

It's also not necessary for the light to interact directly with the dye molecules to cause bleaching: depending on what other molecules are present with the dye (solvents, etc), these other molecules may produce reactive species that then react with the dye.

The action of light on dyed fibres:

About 16,000 published commercial light-fastness assessments have been examined statistically, and from the results the following general rules are formulated, which apply to most dyed fibres

(a) On different fibres the fastness of a dye is higher the higher the regain of the fibre, provided that this is greater than about 4% (i.e. the value for nylon). Thus dyes are usually faster to light on viscose rayon than on cotton, on cotton than on nylon, on wool than on silk, and on secondary cellulose acetate than on cellulose triacetate or nylon

(b) The above rule is reversed with fibres having regains below about 4%, i.e. with the newer synthetic fibres: with these the fastness is usually higher on the fibre of lower regain.

(c) Fastness is often reduced by (i) solid foreign materials in the fibre, e.g. dulling agents or the resin used in crease-resist finishes; or (ii) either cationic surface-active agents or powerfully hydrogen-bonding compounds, e.g. phenols or urea, used as dyeing assistants or after treating agents.

(d) The increase in light fastness with increase in depth of any dye is usually greater the higher the regain of the fibre: it tends to be higher with dyes which are insolubilised in the fibre than with water-soluble ones. The increase in average fastness for a whole class of dyes for a tenfold increase in depth is usually about 1½ units for water-soluble, disperse, and vat dyes, and about 3 units for azoic and sulphur dyes.

The effects summarised by these general principles are considered to be the result mainly of differences in the physical form of the dyes in the fibres, chemical action being important only in a few special cases, e.g. the effect of titanium dioxide delustrant.

There is, however, a more general chemical influence which affects comparisons between certain fibres. This is the difference between the chemical nature of fading on protein and that on non-protein fibres reduction and oxidation respectively which has some effect on the comparative fastness of a given dye on fibres of the two classes, mainly at the upper and lower ends of the scale. Thus, dyes of low fastness on a non-protein, e.g. cotton, viscose rayon, cellulose acetate, or nylon, are likely to have a fastness about one or two grades higher on a protein, e.g. wool or silk (and perhaps Ardil fibre); and those of high fastness on a non-protein are likely to be graded one or two units lower on a protein.

Some suggestions are made of means by which light fastness might be improved: e.g. better fastness is more likely to be obtained by eliminating all small dye particles in the fibre than by encouraging larger ones to grow if small ones are also present. This is because the smaller particles tend to fade more rapidly than the larger, and therefore their fading rate determines the fastness grade of the dyed material, which is judged in the earlier stages of fading. Some types of dye molecule likely to exhibit high fastness are suggested.

The reliability of the fastness data is discussed. Fastness assessments given by different manufacturers for the same dye appear to agree for wool dyes, but Continental assessments for dyes on cotton are usually about one unit higher than those given in this country. This is believed to be due to longer periods of sunshine on the Continent.

POSSIBLE QUESTIONS

PART – B (5 X 8 = 40 MARKS)

1. Give a detail account on FBA
2. Explain the mechanism of action of light on dyes
3. Write a note on mechanism of fading
4. Explain the theory and mechanism of FBA
5. Explain the action of light on dyes fibers
6. Give a brief account on classification and applications of FBA
7. Explain the properties and applications of FBA.
8. Give a brief account on identification of dyes on fibers
9. Explain how FBA used in textile industry?
10. Discuss the fading mechanism of dyes and dyed fibers

Questions	A	B	C	D	**ANSWER**
The Fluorescent Brightening agents operate by the phenomena of……..	Fluorescence	Phosphoresence	photoemission	Radiation	**Fluorescence**
………..is the emission of light by a substance	Phosphoresence	photoemission	Radiation	Fluorescence	**Fluorescence**
…………… is also called fluorescence brightening agent	Dyes	optical brightener	Both A and B	None	**optical brightener**
FBA increases the apparent reflectance of the article in the …….. region of the Spectrum	blue-violet	yellow-blue	violet- yellow	blue - violet	**blue-violet**
All FBAs therefore contain a considerable number of……………… bonds	Single bond	conjugated double	triple bond	none	**conjugated double**
Brighteners are commonly added to ………….. to replace whitening agents					**laundry detergents**
Paper brightness is typically measured at ………	457nm	468nm	443 nm	394nm	**457nm**
Paper used for ……………...does not contain optical brighteners	banknotes	student notes	Both A and B	None	**banknotes**
……………. have also found use incosmetics	Dyes	optical brightener	Both A and B	None	**Optical brighteners**
……….most common classes of compounds with this property for fluorescence brightening agent	stilbenes	Anthracene	xylene	toulene	**stilbenes**
………are commonly added to laundry detergents to make the clothes appear cleaner.	Brighteners	colours	Both A and B	None	**Brighteners**
Fluorescent brightening agents (FBAs)are chemical compounds that absorb light in the ultraviolet and violet region	340-370 nm	457-468 nm	394-412 nm	412-429 nm	**340-370 nm**
Detergent whitener is used as………………..	Blueing agents	Redding agents	Greenish agents	None	**Blueing agents**
Paper brightening is used as ………………..	External coating	Internal coating	Both A and B	None	**Internal coating**
Fiber whitening is used as ………………	Monomer melts	Dimer melts	Polymer melts	trimer melts	**Polymer melts**
Textile whitening is added to ………………..	fabric finishes	Synthetic	yarning	None	**fabric finishes**
Color-correcting or brightening additive in advanced cosmetic formulas is used in….	Shampoos	powder	bleaching	colouringf	**Shampoos**
…………... are commonly added to laundry detergents to make the clothes appear cleaner.	Brighteners	colours	Both A and B	None	**Brighteners**
Paper brightness is typically measured at ……………… well within the fluorescent activity range of brighteners	457 nm	468 nm	489 nm	365 nm	**457 nm**
……………. work by absorbing certain wavelengths of light and reflecting or	Dyes and pigments	Dye and metal complexes	Both A and B	None	**Dyes and pigments**
……………….. have also found use in cosmetics.	Dyes	optical brightener	Both A and B	None	**Optically brightened paper**
………. is often not useful in exacting photographic or art applications, since the whiteness decreases with time	Dye molecule	Pigments	compounds	complexes	**Dye molecule**
…………... absorbs a photon, an electron is excited to a higher energy state.	Dyes	Pigments	compounds	complexes	**Dyes**
The electronic structure of the molecule which changes its ……………... properties	Adsorption	Absorption	Chemisorption	Physisorption	**absorption**

Many dyes that absorb visible light have large systems of conjugated double bonds and if these are broken, the absorbance can shift to much ……………	shorter wavelengths	Longer wavelength	High intensity	low intensity	**shorter wavelengths**
…………..tend to be more susceptible to photo bleaching than things like quantum dots and inorganic pigments.	Inorganic dyes	**Organic dyes**	Semi organic dyes	Semi inorganic dyes	**Organic dyes**
The light to interact directly with the ………….. to cause bleaching	Dye molecule	Pigments	compounds	complexes	**dye molecules**
Fastness is often reduced by solid foreign materials in the ………	protein	Protopectinases	Vitamin	Fibre	**fibre**
………..used as dyeing assistants or after treating agents	Aldehyde	ketone	phenols	acid	**phenols**
The increase in light fastness with increase in depth of any dye is usually greater the higher the regain of the ………	protein	Protopectinases	Vitamin	Fibre	**fibre**
FBA additives are often used to enhance the appearance of color of fabric and paper, causing a ………	Blackning effect	whitening effect	Both A and B	None	**whitening effect**
4 4'-bis(benzoxazolyl)-cis-stilbene and 2 5-bis(benzoxazol-2-yl)thiophene used as optical brighteners …..	laundry detergents	Brightning agents	Both A and B	None	**laundry detergents**
………………. derivatives are subject to fading upon prolonged exposure to UV, due to the formation of optically inactive cis-stilbenes.	stilbene	napthalene	anthracene	All the above	**stilbene**
Non-stilbene brighteners are used in more permanent applications such as whitening ………………..	synthetic fiber	natural fibre	Both A and B	None	**synthetic fiber**
Fastness assessments given by different manufacturers for the same dye appear to agree for……………	cotton dyes	wool dyes	Both A and B	None	**wool dyes**
4,4′-diamino-2,2′-stilbenedisulfonic acid is a popular ………	Dyes	optical brightener	Both A and B	None	**optical brightener**
…… can be "boosted" by the addition of certain polyols, such as high molecular weight polyethylene glycol or polyvinyl alcohol.	Brighteners	Darkneres	visible light	sunlight	**Brighteners**
These additives increase the visible ……. emissions significantly.	Orange light	Green light	Blue light	Red light	**Blue light**
…….. can also be "quenched". Excess brightener will often cause a greening effect as emissions start to show above the blue region in the visible spectrum.	Brighteners	Darkneres	visible light	sunlight	**Brighteners**
The difference between the chemical nature of fading on protein and that on .... fibres reduction and oxidation respectively which has some effect on the comparative fastness of a given dye on fibres of the two classes, mainly at the upper and lower ends of the scale	non-protein	protein	Vitamin	Carbohydrate	**non-protein**
………….of a class of aniline dyes that vary from blue to black and are used as stains for nervous tissue and as a negativestain for bacteria and spirochetes.	Nigrosines	Induline	Cyanine	Nitriles	**Nigrosines**
…………main industrial uses are as a colorant for lacquers and varnishes and in marker-pen inks.	Nigrosines	Induline	Cyanine	Nitriles	**Nigrosines**
Sulfonation of nigrosin yields a water-soluble……………	Anionic dyes	Cationic dyes	Both A and B	None	**Anionic dyes**

…….used in tests for viability because living cells exclude the dye, but it enters dead cells.	Nigrosines	Induline	Cyanine	Nitriles	**Nigrosines**
…..used as black pigments, prepared by heating nitrobenzene or nitro-phenol, aniline and phenylammonium chloride with iron filings.	Nigrosines	Induline	Cyanine	Nitriles	**Nigrosines**
…….. is a dye of blue, bluish-red or black shades.	Nigrosines	Induline	Cyanine	Nitriles	**Induline**
……. consists of a mixture of several intensely colored species	Nigrosines	Induline	Cyanine	Nitriles	**Induline**
Induline is a ………………….	Synthetic dye	Natural dye	Both A and B	None	**Synthetic dye**
The indulines are prepared as mentioned above from ……………	aminonitrocompounds	aminoazo compounds	Both A and B	None	**aminoazo compounds**
The indulines may be subdivided into …………….. Groups	2	4	6	8	**4**
The rosindulines and naphthindulines have a strongly ……………. character	basic	acidic	neutral	None	**basic**
The rosindulines and naphthindulines have a ……………. Colour salts	Blue	Green	Red	Orange	**Red**
Benzinduline (aposafranine), $C_{16}H_{13}N_3$, is a ……………	Strong acid	Weak acid	Strong base	Weak base	**Weak base**
………... is obtained from quinone dichlorimide and phenyl-13-naphthylamine	naphthinduline	rosinduline	Isorosinduline	Benzinduline	**Isorosinduline**
………... is obtainedfrom benzeneazo-a-naphthylamine and aniline	naphthinduline	rosinduline	Isorosinduline	Benzinduline	**rosinduline**
……….. is obtainedfrom benzeneazo-a-naphthylamine and naphthylamine.	naphthinduline	rosinduline	Isorosinduline	Benzinduline	**naphthinduline**
Cyanine is the non-systematic name of a ……….. family belonging to polymethine group	synthetic dye	natural dye	Both A and B	None	**synthetic dye**
………... reagents can be used in purely aqueous conditions	Sulfo-Cyanine	Nitro-Cyanine	Bromo-Cyanine	Chloro - cyanine	**Sulfo-Cyanine**
Sulfonated cyanines are ………….	Soluble	Insoluble	Partially soluble	Soluble whie heating	**Insoluble**

90 copies

Reg. No…………………

[15CHU603B]

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Under Section 3 of UGC Act 1956)
COIMBATORE-641 021
(For the candidates admitted from 2015 & onwards)

III B.Sc. Chemistry
INTERNAL EXAM I
ELECTIVE- II DYECHEMISTRY

Time: 2 hours
Date:
Maximum: 50 Marks

PART A (20 x 1 = 20 Marks)
Answer all the questions

1. The two major types of colorants produced today are……….

   a) Dyes and Pigments b) Varnish and Thinner c) Quinones and Anthraquinones d) Complexes and Double salts

2. Dyes are normally ……..soluble.

   a) Oil b) Water c) Acid d) Fat

3. The auxochromes are groups that cannot undergo ….. ..transitions.

   a) π-π^* b) n- π c) π- π d) non-bonding

4. The combinations of specific chromophore-auxochrome are termed as………

   a) Chromogen b) Ionisation c) Absorption d) Chemisorption

5. …. … do not interact with the textile substrates.

   a) Metal complex b) Varnishes c) Pigments d) Dyes

6. The chromophore present in nitrobenzene is………

   a) C_6H_5 b) NO_2 c) NH_2 d) C_2H_5

7. ……… dyes are used mainly on wool for improved fastness.

   a) Basic b) Acidic c) Organic d) Metal complex

8. Natural dyes are made from …………… . and .. …………

   a) Plants and Minerals b) Coal tar and Petroleum c) Plants and Coal tar d) Minerals and Coal tar

9. Dyes are …….which are widely used for imparting colour to textiles.

   a) Inorganic compounds b) Organic compounds c) Acidic compounds d) Basic compounds

10. …….is the leading fibre in Textile Industry.

    a) Nylon b) Cotton c) Wool d) Wood

11. ……….of cotton textiles is an essential treatment in textile.

    a) Packing b) Scouring c) Grinding d) Welding

12. ………..is the solubilisation of insoluble protopectin and give rise to highly polymerized soluble pectin.

    a) Protein b) Protopectinases c) Vitamin d) Fibre

13. ……..are soluble in water and are applied under acidic conditions.

    a) Acid dye b) Vat dye c) Basic dye d) Fibre

14. Dyes effluent largely consists of …. ..and coloured in nature.

    a) dye intermediates b) organic compounds c) inorganic salts d) nano particles

15. Nitration reaction is carried out by the mixture of .

    a) Con. HCl + Con. HNO_3 b) Con. HCl + Con. H_2SO_4 c) Con. HNO_3 + Con. H_2SO_4 d) Con. H_2SO_4 + CH_3COOH

16. The textile industry accounts for the largest consumption of ....

a) Gas b) wood c) dyestuffs d) oil

17. 1-napthol – 2 – sulphonic acid is also called as ....

a) Schaeffe's acid b) Nevile – Winther's acid c) Tobias acid d) Cassella acid

18. The process of introducing an amino group in an aromatic nucleus is known as ....

a) Nitration b) Sulphonation c) Acylation d) Amination

19. .... and .... are used as first and end component for the preparation of azo dyes.

a) Tobias acid and Cassella acid b) Bronner acid and Cassella acid c) Bronner acid and Tobias acid d) Cleve acid and Bronner acid

20. Oxidation of anthracene with air in presence of V_2O_5 leads to ....

a) Anthraquinone b) 2-Hydroxyanthraquinone c) 1-Nitroanthraquinone d) Anthraquinone - 2 – sulphonicacid

PART- C (3 x 10= 30 Marks)

21. a) (i) Explain about chromophore, auxochrome and resonance.
(ii) Discuss about the absorption and intensity shifts in UV spectroscopy.

(or)

b) (i) Distinguish between dyes and pigments.
(ii) Discuss about dyestuff intermediates in detail.

22. a) Explain the preparation of dyes using nitration process with four different examples.

(or)

b) Explain the preparation of dyes using sulphonation process with four different examples

23. a) Explain the Classification and properties of direct cotton dyes.

(or)

b) Discuss the dyeing mechanism of direct cotton dyes with suitable example.

Part A

Answer All the questions (20 x 1 = 20 marks)

1. A) Dyes and pigments
2. B) Water
3. A) π-π*
4. A) chromogen
5. C) pigments
6. B) NO_2
7. D) Metal complexes
8. A) Plants and minerals
9. B) Organic compounds
10. B) Cotton
11. B) Scouring
12. B) Protopectinases
13. A) acid dye
14. C) inorganic salts
15. C) Conc HNO_3+ Conc H_2SO_4
16. C) dyestuffs
17. A) schaeffes acid
18. D) amination
19. B) bronner acid and cassella acid
20. A) anthraquinone

Part B

Answer All the questions (3 x 10 = 30 marks)

21. a) (i) Explain about chromophore, Auxochrome and resonance
(ii) Discuss about the absorption and intensity shifts in UV spectroscopy

Chromophore

The partial structures necessary for color (unsaturated groups that can undergo π-π* and n-π* transitions) were called chromophore. C=C, C_6H_6, N=N, $-NO_2$, C=O, -CHO groups are examples for chromphores

Auxochromes

It was also observed that the presence of some other groups caused an intensification of color. These groups are called *auxochromes*. The auxochromes are groups that cannot undergo π-π^* transitions, but can undergo transition of n electrons: -OH, -OR, -NH2, -NHR, -NR2, -X

Resonance

Unlike most organic compounds, dyes possess colour because they 1) absorb light in the visible spectrum (400–700 nm), 2) have at least one chromophore (colour-bearing group), 3) have a conjugated system, i.e. a structure with alternating double and single bonds, and 4) exhibit resonance of electrons, which is a stabilizing force in organic compounds. When any one of these features is lacking from the molecular structure the colour is lost.
Other factors contributing to colour are illustrated.

(ii) Discuss about the absorption and intensity shifts in UV spectroscopy

21. b) (i) Distimguish between dyes and pigments

DYES

(i) A dye or dyestuff may be defined as a coloured organic compound which is used for imparting colour to a substrate.

(ii) Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance.

(iii) The dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied.

(iv) Usually, the substrate is the textile fibre or fibre or fabric. In addition to these, there are other substrates like as paper, leather, plastics, wax, cosmetic base, etc. the non-toxic dyes are used for colouring the food stuffs and drugs. The colour sensitive dyes are used in colour photography.

(v) The color intensity of the dye molecule depends on how strongly it absorbs radiation in the visible region, which extends from 400 to 700 nm.

(vi) A dye is a coloured substance whereas all coloured substances are not dyes. Thus a dye should fix itself on the substrate to impart it a permanent coloured appearance.

(vii) For example, azo benzene is not a dye even if it is red in colour, as it cannot be attached to substrate. However, Congo red is a dye because it can be applied on cotton and retained by it. Thus, the dyes should have certain groups which help the attachment of the fibre.

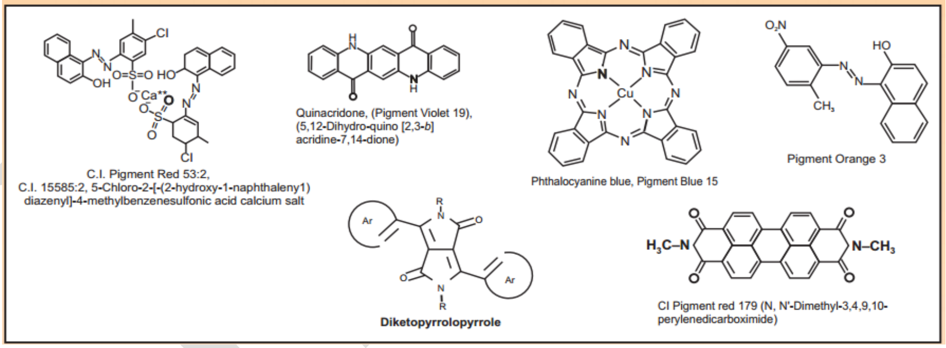
PIGMENT

(i) It is the coloured substance which is insoluble in water or other solvents. It means that the application of dye and pigment will be different.

(ii) A dye is applied in the form of a solution, while the pigment is applied in the form of a paste in a drying oil, in which it is insoluble.

(iii) Pigments both inorganic and organic types, are almost always applied in an aggregated or crystalline insoluble form that requires a binder to form a coating on the surface of a substrate. Pigments do not interact with the substrate and hence do not destroy the crystal structure of the substrate

(iv) There are some colourless compounds which are used as the optical brighteners. They are also known as the white dyes. They have the special property of absorbing ultraviolet light and re-emitting the visible light so that the fabric appears bright.



Structure of Dyes & Pigments

(ii) Discuss about dyestuff intermediates in detail

- Dyes and dye intermediates industry is an important sector of the Indian chemical industry. This sector has grown at a very fast pace after independence and nearly half of its production is being exported today.
- There is emanating of wastewater from the various operation of the plant. The quantities of effluents generated from various units. The effluents generated during the operations

are mainly from washing and utilities. The pollution that accompallles this industry, its nature and extent is, particularly, because of the non-biodegradable nature of the dyes as well as due to the presence of acid/ alkali/ toxic trace metals/ carcinogenic aromatic amines in the effluents.

- The wastewater generated from dye and dye intermediate industries, mainly have intense colour having various shades like red, blue green, brown and black through the production of different colour containing dyes and usually have high level of COD, BOD, acidity, chlorides, sulphates, phenolic compounds and various heavy metals viz. copper, cadmium, chromium, lead, manganese, mercury, nickel, zinc etc.
- Dyes, as they are intensively coloured, cause special problems in effluent discharge and even small amount is noticeable. The effect is aesthetically more displeasing rather than hazardous, and can prevent sunlight penetration decreasing photosynthetic activity in aquatic environment. Although, some azo dyes that cause theeffluent colour, have been implicated as being mutagenic/ carcinogenic as well as toxic to aquatic life.

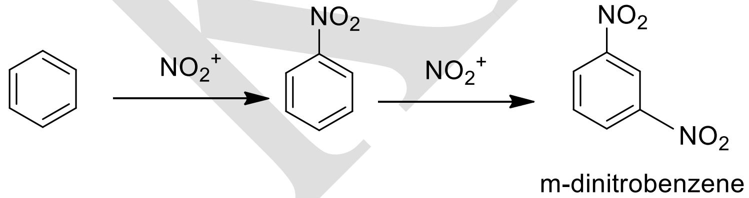
22. a) Explain the preparation of dyes using nitration process with four different examples.

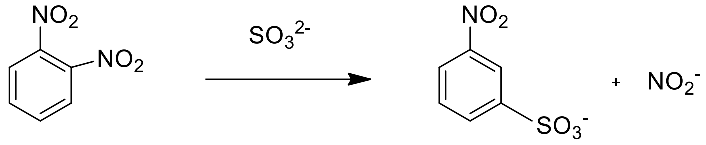
$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

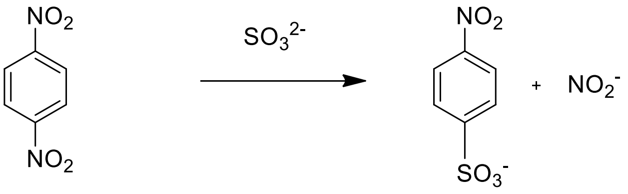
$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O+ + 2HSO_4^-$$

Preparation of nitro compounds used in dyestuff industries

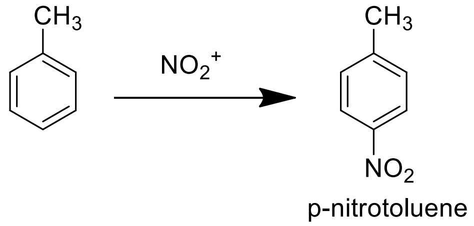
1. **m-Dinitrobenzene**

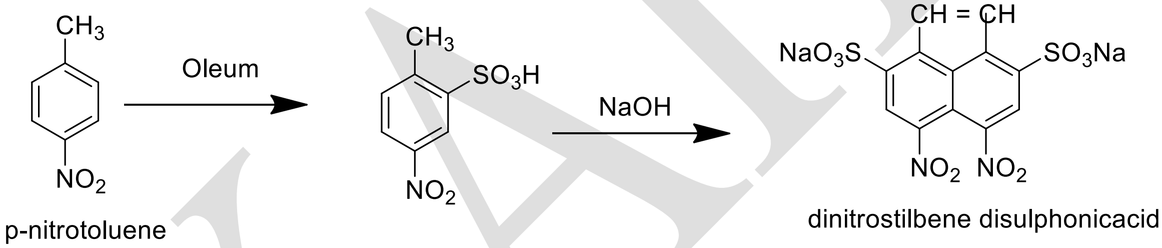






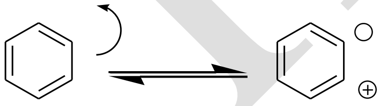
2. p-Nitrotoluene

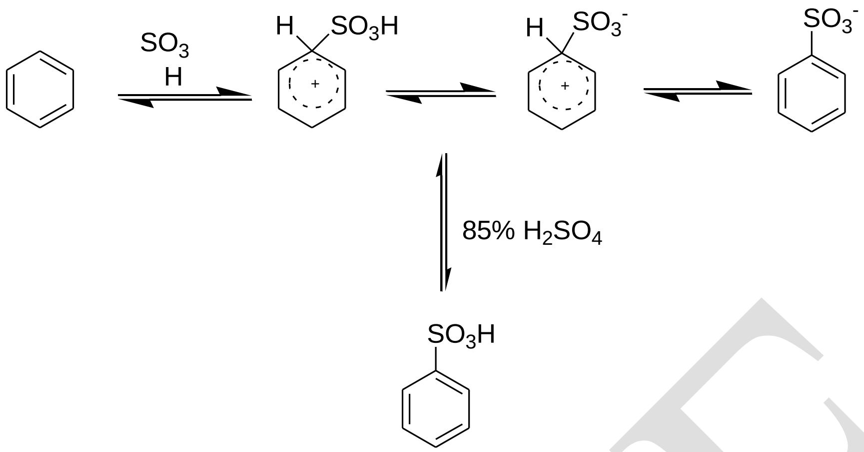




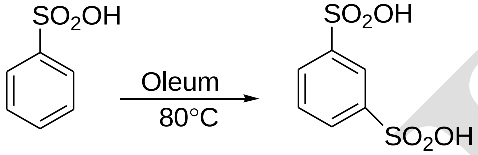
22. b) Explain the preparation of dyes using Sulphonation process with four different examples.

$$2H_2SO_4 \rightleftharpoons H_3O_+ + HSO_4 + SO_3$$



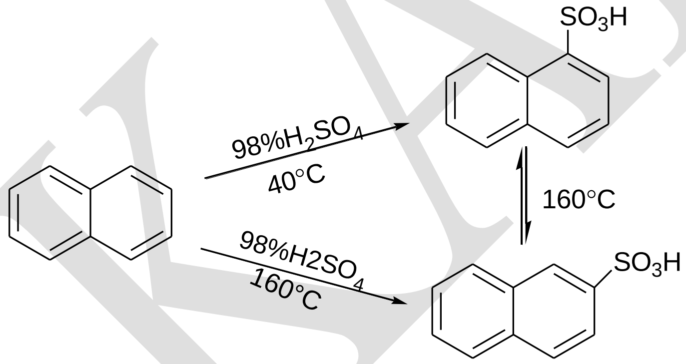


Sulphonation of Benzene:

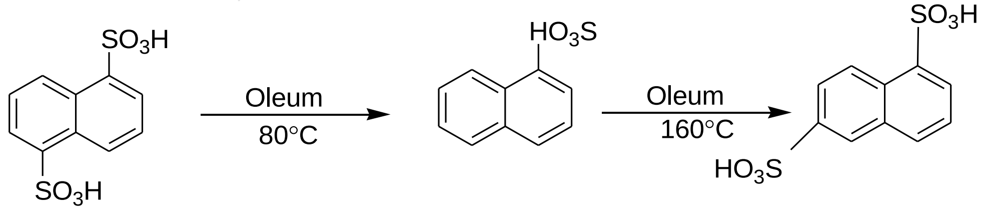


Sulphonation of Naphthalene:

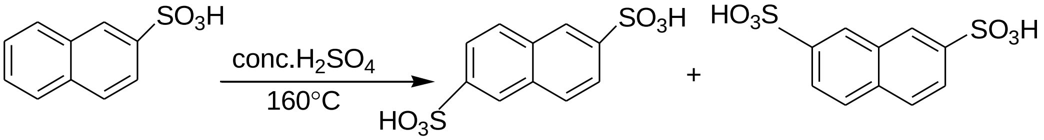
(a)Naphthalene-1-Sulphonic acid



Naphthalene-1,5disulphonic acid Naphthalene-1,6-disulphonic acid

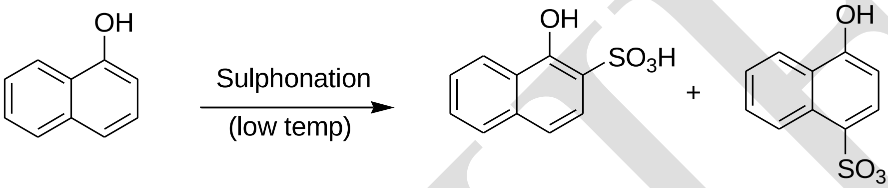


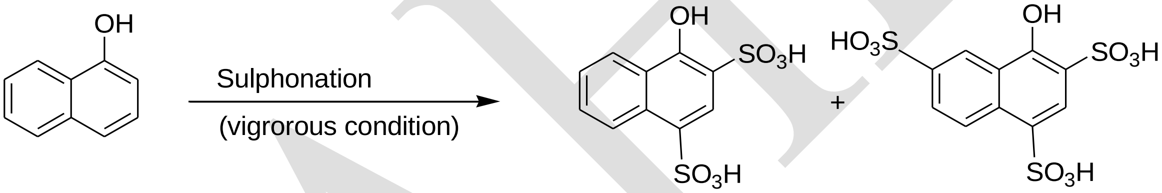
Naphthalene -2, 6-disulphonic acid and Naphthalene -2,7-disulphonic acid.



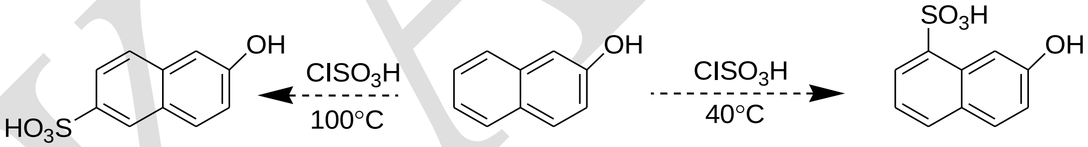
Sulphonation of Naphthol

(a)Sulphonation of α-naphthol or 1-naphthol.





(b)Sulphonationof β-naphthol or 2-naphthol

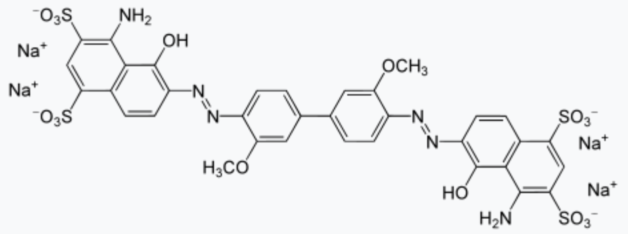


23. a) Explain the classification and properties of direct cotton dyes

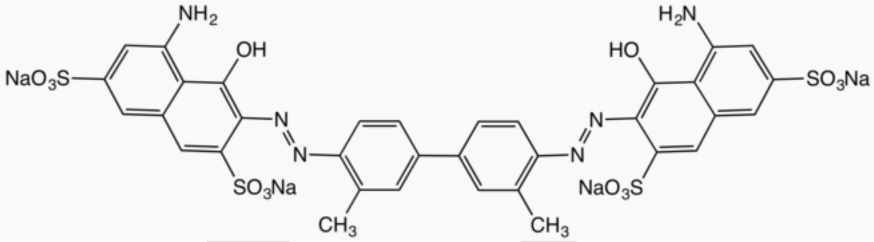
A substantive dye or direct dye is a dye that adheres to its substrate, typically a textile, by non-ionic forces. The amount of this attraction is known as "substantivity": the higher the substantivity the greater the attraction of the dye for the fiber. Substantive dyes work best on textiles with high contents of cellulose, such as cotton. In contrast to direct dyes, wool and leather goods are dyed by the process of ion exchange, exploiting the cationic nature of proteins near neutral pH. The development of substantive dyes helped make mordant dyes obsolete.

Substantive dyes are set in a slightly basic or neutral environment at temperatures close to boiling point. They are set by formation of aggregates of dyes within interstices of the fibres. Aggregation is enhanced by extended aromatic rings.

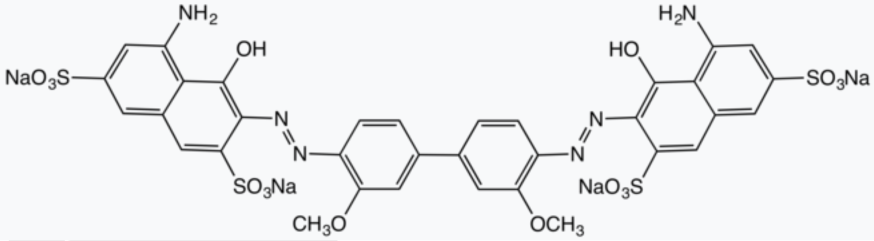
Representative direct dyes



Direct Blue 1.



Trypan blue (Direct Blue 14), which also exhibits medicinal properties.



Direct Blue 15.

A water-soluble dye usually of the azo class that is used in alkaline or neutral solution especially for dyeing cellulosic material (such as cotton or paper) directly

Major types of Direct Dyes

There are two major types of Direct Dyes:

Anionic Direct Dyes

Anionic Direct Dyes are used for coloring papers, controlling tint and shade and correction of two sided paper color. The main structural features of the Anionic Direct Dyes are: the planar vary from each other, the structural single and double bonds are very much extended, and contains one or more than one sulfonate groups. These sulfonate groups make them soluble in the water.

Cationic Direct Dyes

The main structural features of cationic direct dyes are : λ the structural single and double bondings are extended. λ the molecular structure is planar λ positive charges are more than the negative charges

Properties of direct dyes Direct dyes have some characteristics. Followings are tha main properties of direct dyes.

- Direct dyes are water soluble dyes.
- It is anionic in nature.
- It needs electrolyte for exhaustion.
- Dyeing process is carried out in alkaline condition.
- Generally applied for cellulosic as well as protein fibers.
- Fastnees properties are improved by after treatment. λ It is not widely used as compared with reactive dyes.
- Comparatively cheap in price.
- Direct dyes are used for cheap goods for local market.

Chemicals Nature of Direct Dyes Chemically they are salts of complex sulfonic acids. Structure:-More than 75% of all direct dyes are unmetallised azo structures, great majority of them are disazo or polyazo types.

Ionic Nature:-Their ionic nature is anionic.

Solubility:-They are soluble in water .

Affinity:-They have an affinity for a wide variety of fibers such as cotton ,viscose, silk jute ,linen etc.. They do not make any permanent chemical bond with the cellulosic fibers but are attached to it via very week hydrogen bonding as well as vander waals forces. Their flat shape and their length enable them to lie along-side cellulose fibers and maximize the Van-der-Waals, dipole and hydrogen bonds

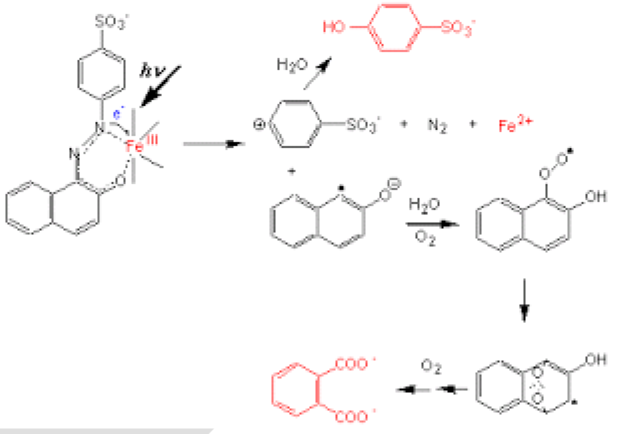
Dyeing Method The color is pasted well and dissolved in boiling water to get a lump free solution .An addition of 0.5–2 g l–1 sodium carbonate may be advantageous when applying dyes of only moderate solubility in full depths.

The dye bath is set at 40°C, λ Raise to the boil at 2 degC min–1 Hold at the boil for 30–45 min, λ during hold add 10–15 g l–1 of sodium chloride or calcined Glauber's salt. Light shades are dyed without or lesser addition of salt. λ Improved yields can be achieved when applying full depths by cooling to 80°C at the end of the period at the boil, adding a further 5 g l–1 salt and rising to the boil again

λ Dye bath variables which must be considered for level dyeing, 1.Temperature of Dyeing and rate of heating 2.Electrolyte concentration and addition 3.Time 4.Dye solubility 5.Use of leveling agent

23. b) Discuss the dyeing mechanism of direct cotton dyes with example

Mechanism of dyeing



Affinity

It is the difference between the chemical potential of dye in its standard state in the fiber & the corresponding chemical potential in the dye bath i.e. tendency of a dye to move from dye bath into a substance. It is expressed in Joule or cal (per mole) and quantitative expression of substantivity.

Substantivity

The attraction between a substrate and a dye or other substance under the precise condition of test whereby the test is selectively extracted from the application medium of substrate. It is the qualitative expression of affinity. Substantivity depends on temperature, type of fiber, electrolyte concentration. Substantive dyes have affinity and are soluble.

Reproducibility of Shades

The shade of the dyes should be reproducible when required. Certain dyes have ability to overcome the factors like liquor ratio, pH, temperature etc. which affect the reproducibility. Characteristics of highly reproducible dyes are:

- Highly soluble
- Medium substantivity
- Medium reactivity
- Good wash off properties
- Highly diffusible

Optimization of Dye

The principle is to carry out dyeing in a manner in which the dyestuffs absorbed by substrate almost uniformly with less dye wastage.

1.Substrate

- Affinity
- Circulation speed
- Action of chemicals before

2.Dyestuff

- Depth of shade
- Optimum quantity/yield
- Diffusion ability and regularity
- Color fastness
- Combination & mixability
- Chromphore percentage

3.Auxiliary Products

- Optimum quantity
- Compatibility with dyestuff and with each other
- Levelness
- Control of PH in final exhaustion
- Reproducibility
- No adverse effect

4. Temperature and time

- Low initial temperature to avoid rapid absorption of dye
- Control of critical temperature zone for maximum exhaustion
- Sufficient time for penetration and fixing

5. Machine

- Control of batch
- Volume of flow
- Temperature regulation

The actual dyeing theory can be obtained mathematically from kinetics of dyeing or dyeing equilibria. The dyeing phenomena found in principle of dyeing curve. The factors for uniform color & optimization of dye all are related to kinetic phenomena. Therefore kinetic dyeing is important in the dyeing process.