DYES, COLOUR AND CHEMICAL CONSTITUTION

UNIT V DYES

DYES :

Definition :

Dyes are the coloured substances used to colour fabrics, leather, paper, food stuffs etc.

Natural Dyes :

Dyes obtained from the natural sources are called Natural dyes.

Ex. Alizarin, Indigo etc.

Synthetic Dyes :-

Dyes that are prepared by synthetic routes are called synthetic Dyes.

THEORIES OF COLOUR AND COMPOSITION :-

OTTO WITT. the German scientist put forword. his theory of colour and constitution known as. chromophore - Auxochrome Theory.

CHROMOPHORE - AUXOCHROME THEORY :-

1. The colour of the organic compounds is mainly due to the presence of unsaturated group known as chromophore.

(Gr : chroma - Colour ; Phorein - to bear).

The compound bearing the chromophoric group is called chromogen.

Important chromophores are.

a) $-N\begin{matrix}=O\\ \rightarrow O\end{matrix}$ Nitro

b) $-\ddot{N}=O$ Nitroso

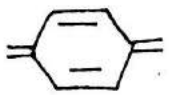
c) $-\ddot{N}=\ddot{N}-$ Azo.

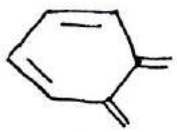
d) $-\ddot{N}=\overset{|}{N}\rightarrow O$ Azoxy

e) $\overset{|}{C}=O$ Carbonyl

f) $-\overset{|}{C}=S$ Thio Carbonyl.

g) $-\overset{|}{C}=\overset{|}{C}-$ Ethylenic

h)  P-Quinonoid

i)  o-Quinonoid.

(2). The greater the no of chromophores in a chromogen. The greater is the intensity of the colour in the of chromogen. The effect is particularly marked when the chromophore groups are in conjucation with one another.

Ex

(a) colour changes in diphenyls, $C_6H_5(CH=CH)_nC_6H_5$

$C_6H_5CH=CHC_6H_5$ is colourless.

$C_6H_5(CH=CH)_2C_6H_5$ is colourless

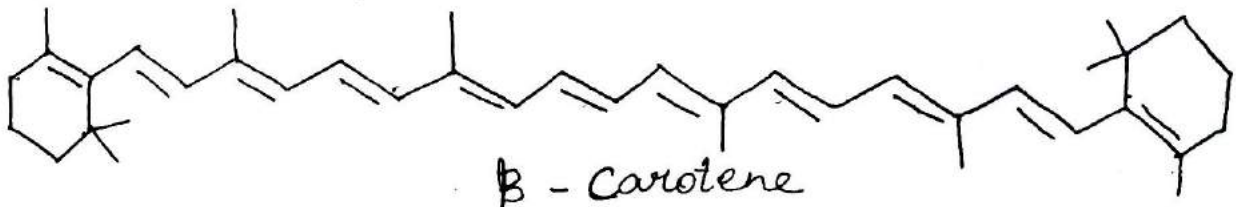
$C_6H_5(CH=CH)_3C_6H_5$ is pale yellow.

$C_6H_5(CH=CH)_4C_6H_5$ is yellow.

$C_6H_5(CH=CH)_5C_6H_5$ is orange.

↓ Deepening in colour.

(b) Ethylene :- 1,3-butadiene and 1,3,5-hexatriene are colourless but β-carotene (orange yellow pigment to which carrots owe their colour) with an extensive conjucation of carbon-carbon double bonds is orange red.



β-Carotene

(c) Certain substituents fail to produce colour by themselves but they deepen the colour due to the chromophoric system already present. such substituents are termed as auxochromes. The main auxochromes arranged in order of decreasing effectiveness are

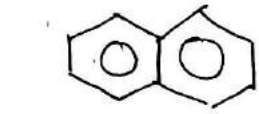
$-\ddot{N}R_2 > -\ddot{N}HR > -\ddot{N}H_2 > \ddot{O}H >$ Halogens $> -\ddot{O}R$

← colour deepening ——

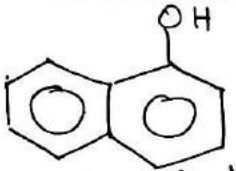
Even alkyl groups exert auxochromic effect though of a lower order.

Examples :-

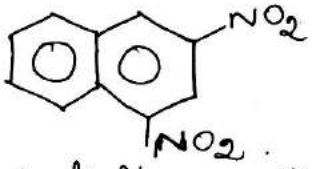
ⓐ Napthalene and Napthol are colourless, 2,4-dinitronapthalene is pale yellow in colour but not a dye while 2,4-dinitro-1-Napthol bearing -OH (auxochrome) is an orange red dye.



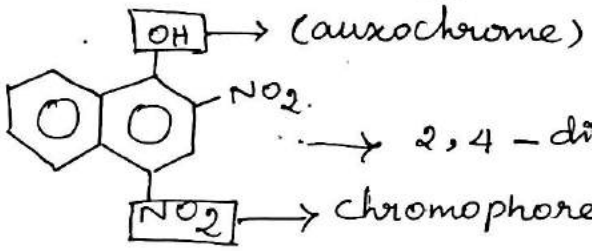
Napthalene (colourless)



1-Napthol (colourless)



(2,4-dinitro napthalene) (Pale yellow)

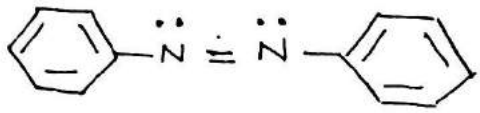


→ 2,4-dinitro-1-naphthol. (orange red dye)

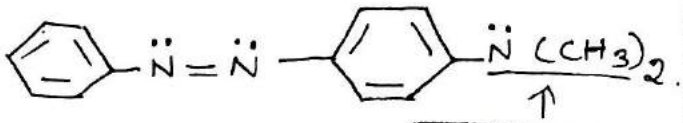
Auxochrome -OH has not only increased colour of the chromogen (2,4-dinitronapthalene) but also facelitate it to act as a dye by fixing the colour to the fabric via hydrogen bonding during the process of dyeing.

ⓑ The auxochromoes are generally salt forming groups and perform two functions namely deepening the colour and providing the necessary requisite for a chromogen to act as a dye. For example, the chromogen azobenzene is almost colourless but p-dimethylamino azobenzene is a familiar dye.

butter yellow due to auxochrome $-\ddot{N}(CH_3)_2$.



Azobenzene
(colourless)



P-dimethylamino Azobenzene
(yellow dye)

A dye may be defined as a chromogen containing an auxochrome. A dye must in addition, posess certain other groups (Ex. SO_3H to impart water solubility) also.

Dye = chromogen + auxochrome.

The colours of organic compounds, according to the with theory: are explained in terms of the types and positions of the chromophores and auxochromes present in a molecule, the more the chromophores there are and the longer the conjucated system in a molecule is, the deeper will be the colour. For a coloured compound to act as a dye, it should have both chromophoric and auxochromic groups

CLASSIFICATION :-

ⓐ Based on Structure :

Dyes are arranged according to the structure and functional group to which the dyes owe their colour. According to this system dyes are classified into.

ⓐ. Azo dyes
ⓑ. Triphenylmethane dyes.
ⓒ. Anthraquinone dyes.
ⓓ. Indigoid dyes.

(e). Xanthen dyes
(f). Acridiene dyes.
(g). Nitro and Nitroso dyes.
(h). fluorescent brightening dyes.

Based on the method of Application :-

The method of applying a dye to a material varies with the nature of the material. There are three types of fibres to be dyed, namely natural (cotton wool). regenerated (e.g. linen, rayon) and synthetic (eg. nylon, terylene) These fibres may be polar (wool, silk) moderately polar (cotton) and non-polar or weakly polar (eg. terylene). The dyes to colour them should have similar polarities as far as possible, The colour so applied must be wash fast too.

① Direct or substantive Dye :-

A compound is classified as a direct dye. if it can be applied directly by immersing the animal / vegetable fibres or cloth in a hot solution of the dye in water, removing excess of the solution and drying it. Direct dyes are subdivided into.

(a) Acid Dyes :-

(a) Acid dyes are sodium salts of sulphonic acid Nitrophenols. (Eg) Napthol-yellow & Manitus yellow

(b). They can readily dye animal fibres (wool and silk) and nylon but not vegetable fibres.

(c). wool and silk are dyed by dipping in the solution of acid dyes in an acidic bath.

(d). Dyeing takes place directly by the interaction of the polar acidic group of the dye with the basic group of the fibre.

(B) Basic Dyes :- (Malachite green, magenta etc).

(1). Basic dyes are the salts of colour bases with HCl & $ZnCl_2$.

(2). Basic dyes can be animal fibres directly and vegetable fibres often they have been mordanted with tannin.)

2. MORDANT OR ADJECTIVE DYES :

(a). Certain dyes (e.g. Alizarin) fail to dye the fabric directly but they can produce the wash fast colours with the aid of other agents known as mordants and such dyes are known as mordant dyes.

(b). The mordant include the salts of metals like aluminium, iron and chromium and acidic substances like tannic acid depending upon the nature of the dye.

(c). Acid dyes require mordants of metallic oxides where as basic dyes needs acidic mordants.

(d). The fabric is mordanted by dipping in the solution of the mordant and then dipped in the solution of the dye when coloured lake is produced which is insoluble.

(e). Alizarin and Anthraquinone dyes are applied in this manner.

3. DEVELOPED OR INGRAIN DYES :-

(a). Excellent quicke fast colours can be produced by forming the dye directly in the fibre itself by the reaction such as azo - coupling.

(b) The fabric is soaked in the alkaline solution of phenol, dried and then immered in an ice cold solution of diazonium salt, when the azodye is directly developed on the fibre itself (c). such dyes known as developed dyes is called ice - colours. because such dyes are followed at low temperatures within the fabric.

(d). These dyes are particularly useful in making the printed fabrics.

4. VAT DYES :-

(a). Since, they are insoluble coloured compounds on reduction with the sodium hyposulphite, they are converted into alkali soluble white or colourless compounds known as leuco compounds. The colourless leuco form is readily adsorbed by the animal and vegitable fibres.

(b). So, the colourless leuco form of the dye is first introduced into the fabric ~~acid~~ and then the insoluble dye is formed in situ (by oxidation). such dyes are called vat dyes.

(c). Vat dyes in the leuco condition dye both animal and vegetable fibres directly but they are mostly used for cotton fibres.

indigo is an outstanding example.

(5) Metal complex dyes:-

These are prepared as complexes which are then applied to the fibre.

(6) Sulphur dyes:-

These are used mainly with cellulosic fibres.

(7) Disperse dyes:-

They are water soluble dyes which are dispersed by suitable reagents before application to synthetic fibres.

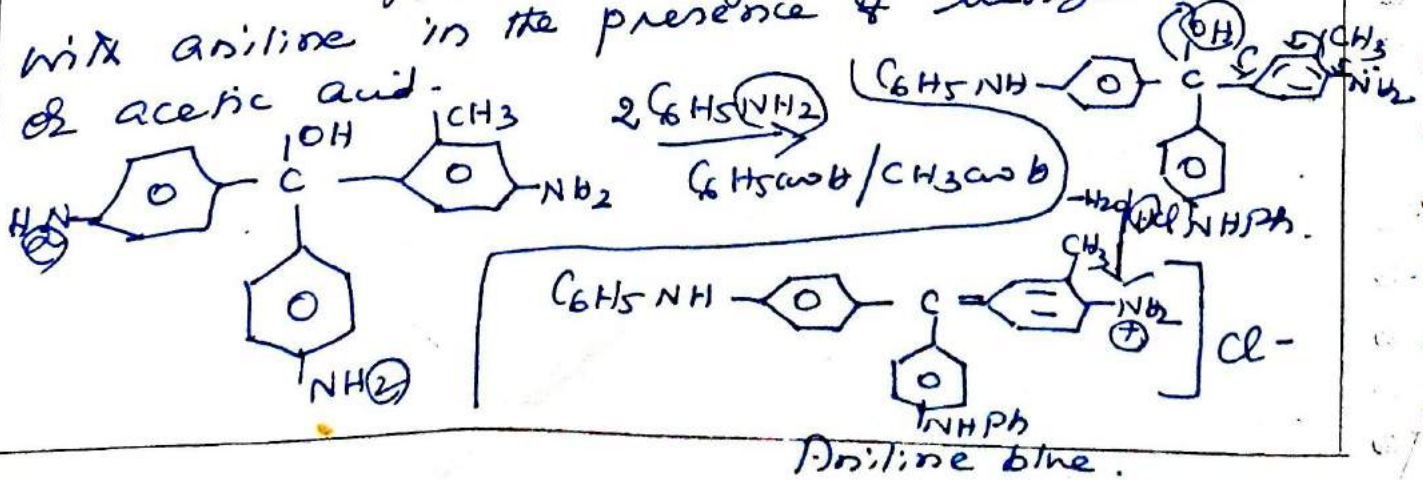
(8) Organic pigments:-

They are water insoluble compounds which are used as colouring agents in paints etc; and when made water soluble they are used as dyes.

ANILINE BLUE:- (Diphenyl rosaniline).

Preparation:-

Rosaniline dye base is heated with aniline in the presence of benzoic acid & acetic acid.



Aniline blue.

II Depending upon the mode of application:- (4)

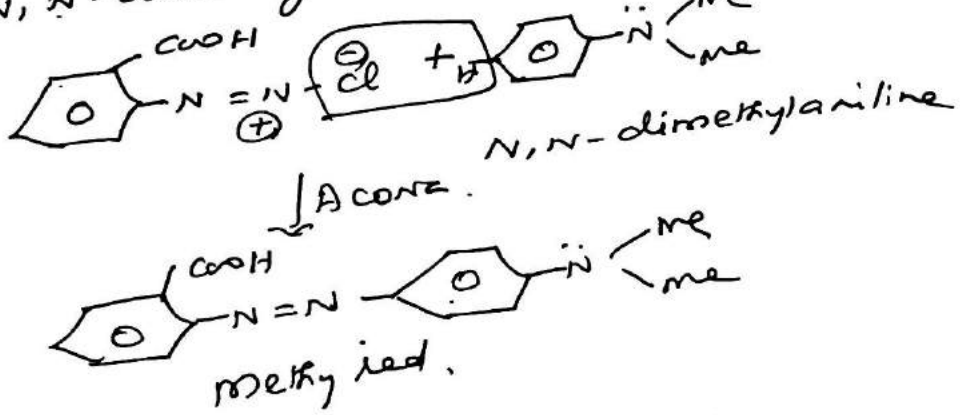
Depending upon its application, azo dyes are classified into

(a) Acid Azodyes :- (Eg) Methyl Orange
(b) Basic " :- (Eg) Bismark brown
(c) Direct " :- (Eg) Congo Red.
(d) Mordant " :- (Eg) Azochrome.

Methyl red:-

Preparation:-

This acid dye can be prepared by coupling diazotised o-aminobenzoic acid with N,N-dimethylaniline in the presence of sodiumacetate.

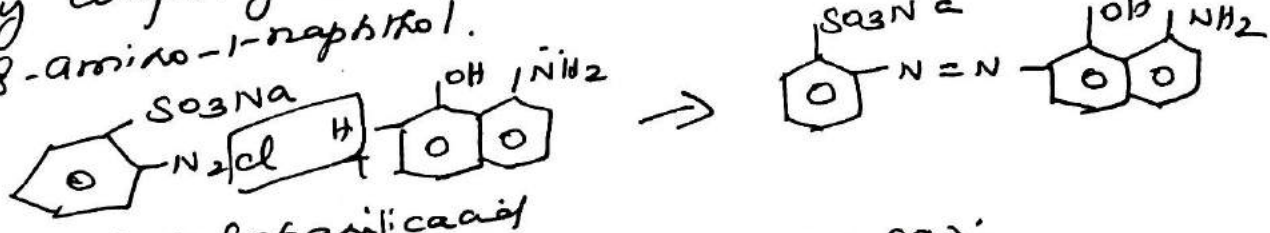


Methyl red.

FAST RED OR PROCION RED:-

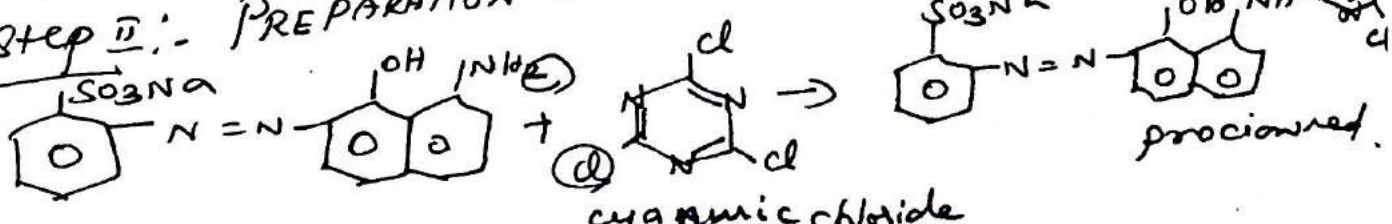
Step I:- Preparation of monoazodye:-

The monoazodye is prepared first by coupling orthosulphanilic acid with 8-amino-1-naphthol.



orthosulphanilic acid

Step II:- PREPARATION OF PROCION RED:-



cyanuric chloride

procionred.

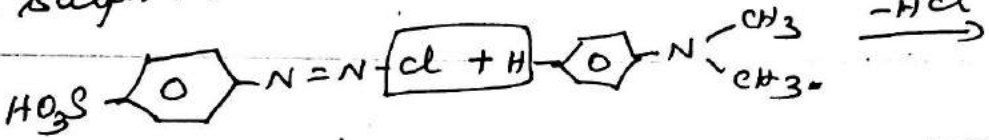
USES:-

These dyes react with free OH groups or the cotton or free $-NH_2$ groups of the wool to give excellent wash-fastness. The colours are generally more brilliant than mordant or polyazodyes.

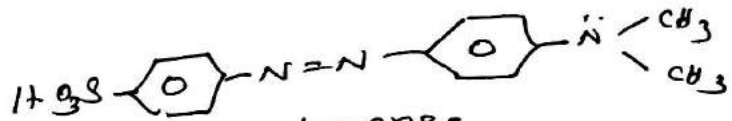
METHYL ORANGE:- (Monoazodye:-)

Preparation:-

It is prepared by coupling diazotised sulphanilic acid with dimethylaniline.



Diazotised sulphanilic acid

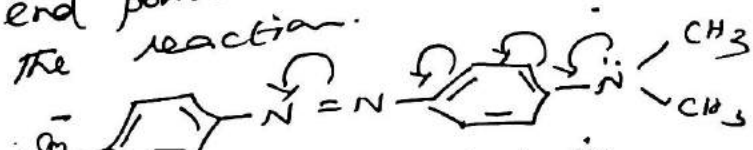


methyl orange.

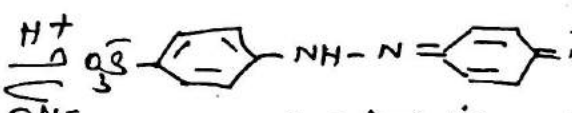
USES:-

① It is an acid dye. It dyes wool and silk and imparts the orange colour but the colour is not fast to light or washing.

② It is used as an indicator in acid-base titrations. It gives yellow colour with alkali and pink colour with acid. The change in colour at the end point is due to the change in the structure of the reaction.



yellow colour in alkali solution



Pink colour in acid solution.

MALACHITE GREEN:- TRIPHENYL METHANE DYES:-

These dyes are $-NH_2$ and $-NR_2$ substituted derivatives of triphenylmethane. These compounds first formed are usually colourless called leuco bases. On oxidation, they are converted into colourless carbinol bases. The carbinol bases readily changes from their benzenoid structure to coloured quinonoid structure in acid by salt formation.

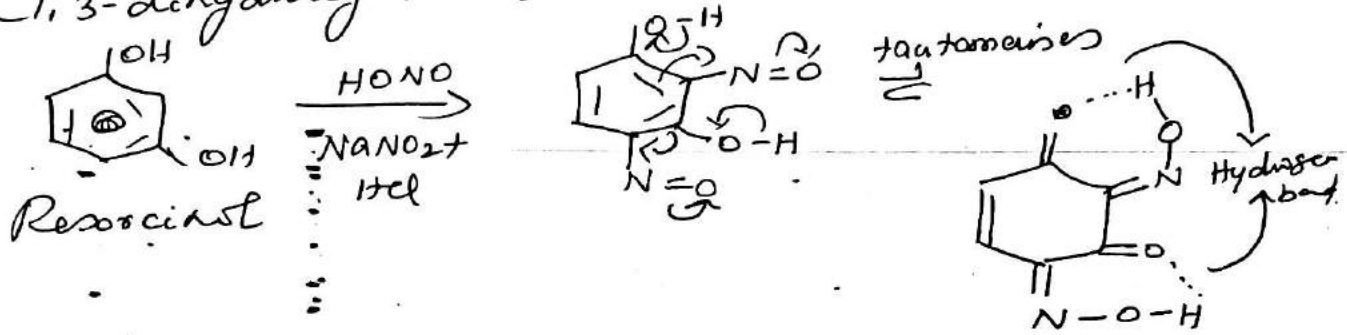
Leuco base (colourless) $\underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}}$ Carbinol base (colourless) $\underset{OH^-}{\overset{H^+}{\rightleftharpoons}}$ Dye Quinonoid Structure (II)

NITROSO DYES:-

These are nitroso derivatives of phenol.

FAST GREEN O

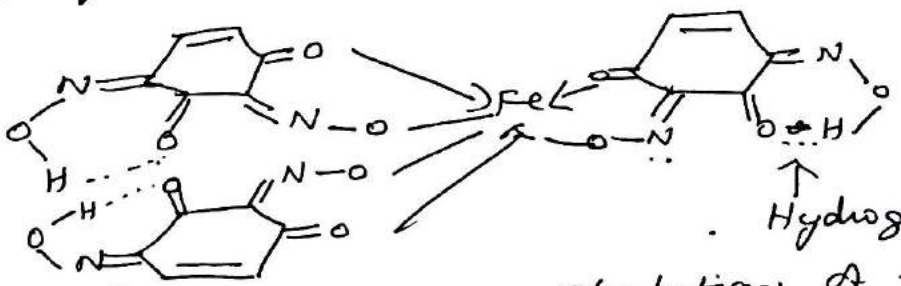
This mordant dye is obtained by the reaction of nitrous acid on resorcinol (1,3-dihydroxy benzene).



Fast Green O.
(Quinonoid form.

Uses:-

The quinonoid oxime (C=N-OH) forms green lakes with ferric ions.



Green lakes due to chelation of Fast green O with Ferric ions.

AZO DYES:-

Azo dyes are characterised by the diazo group $-N=N-$. Here chromophore is an aromatic system joined to the azo group and the common auxochromes NH_2, NR_2 / OH. They are prepared by direct coupling between a diazonium salt and a phenol or an amine

Azo dyes are classified into monoazo, bisazo and trisazo dyes on the basis of number of azo groups present in their structure.

What are azo dyes? How are they classified?

Azo dyes are characterised by the diazo group (-N=N-) with one or more aromatic rings (benzene or naphthalene or SO_3H group (to impart water solubility to the dye) and one or more hydroxyl groups or amino groups. They are prepared by the coupling of suitable diazonium salts with phenols or aromatic amino compounds.

CLASSIFICATION:-

I. ON THE BASIS OF NUMBER OF AZO GROUPS PRESENT:-

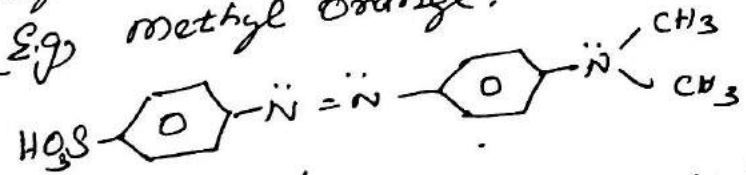
They are subdivided into monoazo, bisazo, trisazo on the basis of number of azo groups in their structure.

(1) MONOAZO DYES:-

(a) Aniline blue
(b) Methyl orange
(c) Methyl red
(d) Butter yellow
(e) Acid orange
(f) Resorcinol yellow
(g) Para red
(h) Paraciaw red.

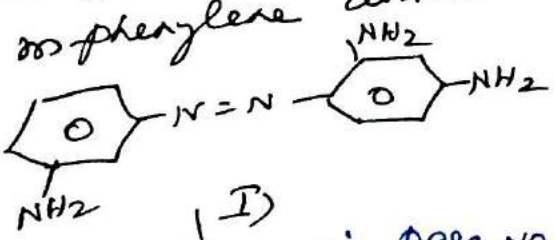
All the above monoazodyes contain a single azo group in their structures.

(Eg) Methyl Orange.

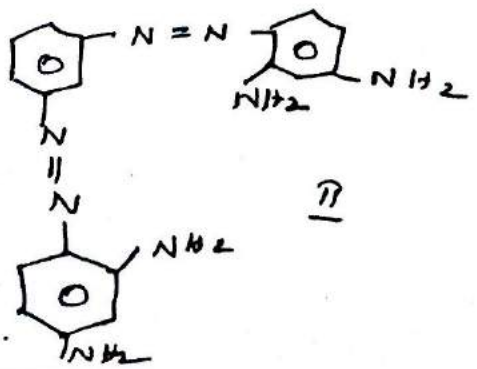


(2) Bisazodyes:-

It is really a mixture of monoazodye(i) and bisazodye (ii) and is got by the coupling of diazotisation of m-phenylene diamine and m-phenylene diamine in excess.



(I)



(II)

(Continuation in page NO: 14 & last page)

Leucobase $\underset{\text{Reduction}}{\overset{\text{Oxidation}}{\rightleftharpoons}}$ Carbinol base $\overset{H^+}{\underset{OH^-}{\rightleftharpoons}}$ Dye

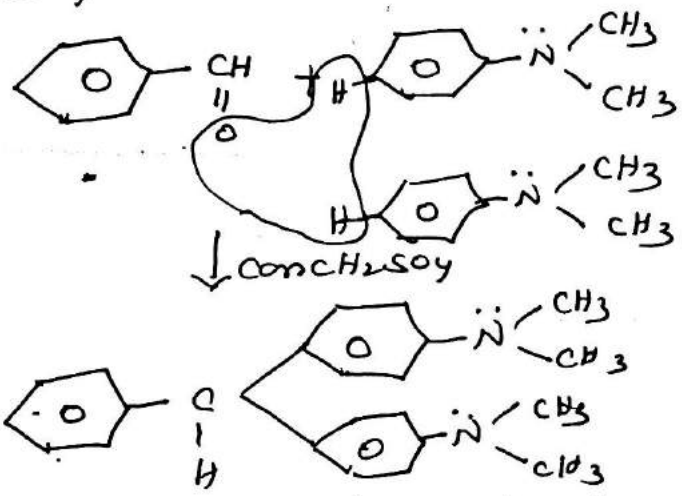
(colourless) (colourless) (Quinonoid structure) coloured.

(continuation in the last page. page No: 14)

- MALACHITE GREEN:-

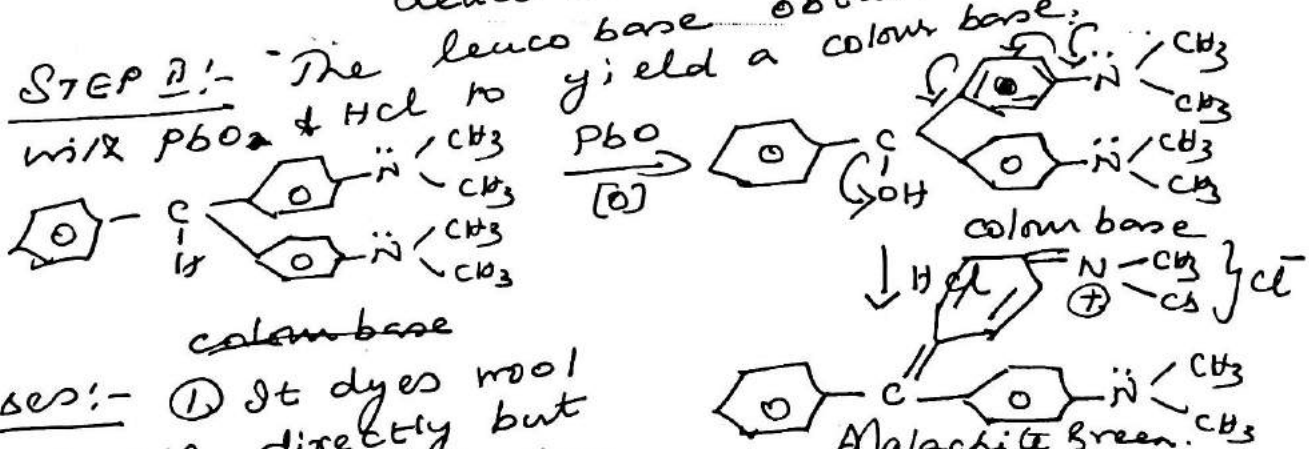
Preparation:-

STEP I :- One molecule of benzaldehyde is condensed with two molecules of dimethylaniline in the presence of conc H_2SO_4.



Leuco base.

STEP II :- The leuco base obtained is oxidised with PbO + HCl to yield a colour base.



Uses:- ① It dyes wool and silk directly but cotton after mordanting with tannin.

② Used for staining bacterial spores with safranine as a counter stain.

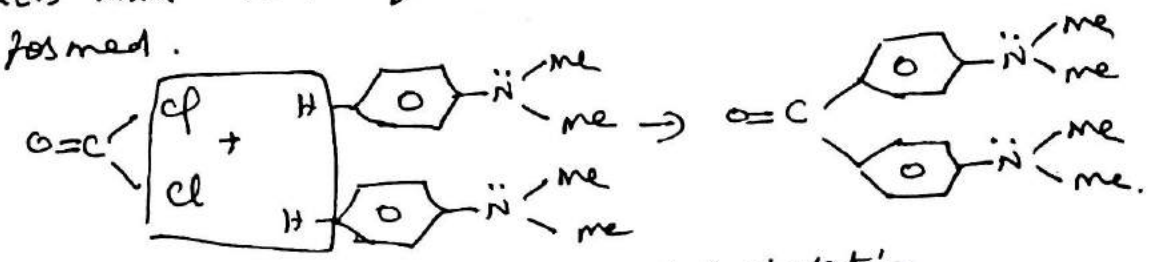
③ Used as a spot test reagent for detecting sulphurous acid and cerium.

④ Used as an antiseptic for bacterial and mycotic infection.

CRYSTAL VIOLET:- (Basic Violet 3)

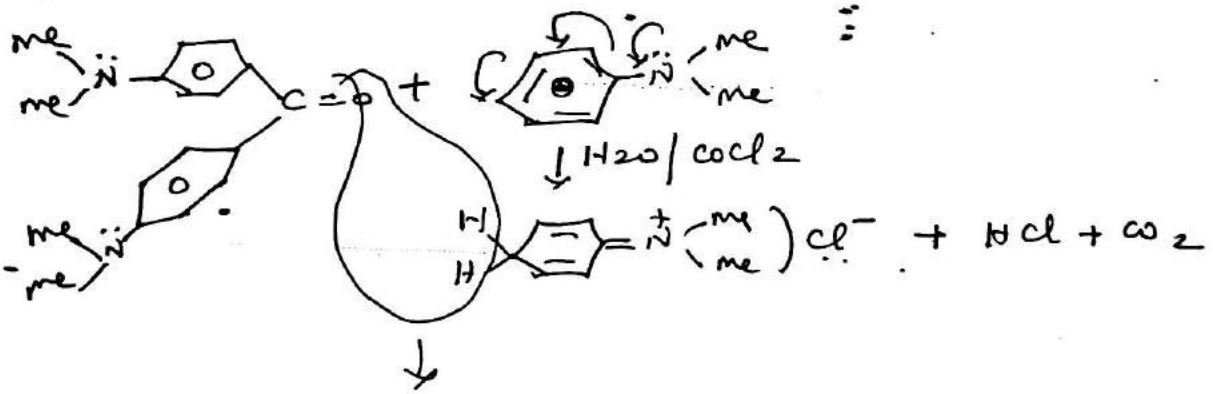
STEP I :- PREPARATION OF MICHLER'S KETONE:-

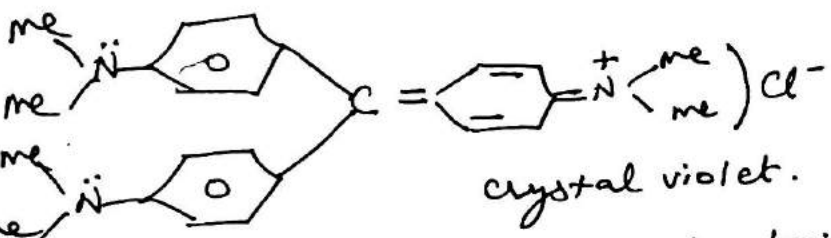
Two molecules of N,N-dimethylaniline reacts with carbonyl chloride and Michler's ketone is formed.



STEP II :- Preparation of crystal violet:-

Michler's ketone is heated with N,N-dimethylaniline in the presence of phosphoryl chloride or carbonyl chloride. It = $COCl_2$ is used Michler's ketone as self generated.





crystal violet.

USES:- ① It is used for bacteriological work and for histological purposes.
② Under the name, Gentian violet, it is used as antibacterial & antifungal agent and internally also in certain infection.
③ It is used in the manufacture of inks, stamping pads and typewriter ribbons.
④ It is also used as an indicator for the determination of hydrogen-ion concentration of solutions.

Azo dyes - classification - continuation :-

III Monoazodyes are subclassified into cationic & anionic dyes & mordant dyes.

(i) Anionic dyes / acidic azo dyes :-

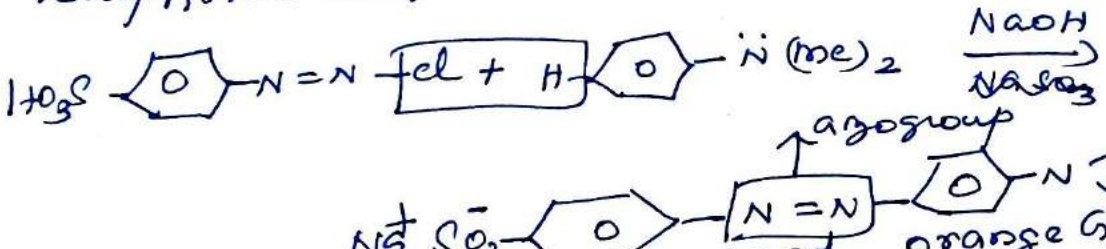
(a) These dyes are characterised by the presence of acidic group such as SO_3H, COOH or phenolic OH group.

(b) This acidic group makes the dye more soluble and also used as the reactive point for fixing the dye.

(c) The acidic group acts as an auxochrome in these dyes.

(Eg) Methyl orange.

It is prepared by coupling diazotised sulphanilic acid with dimethyl aniline.

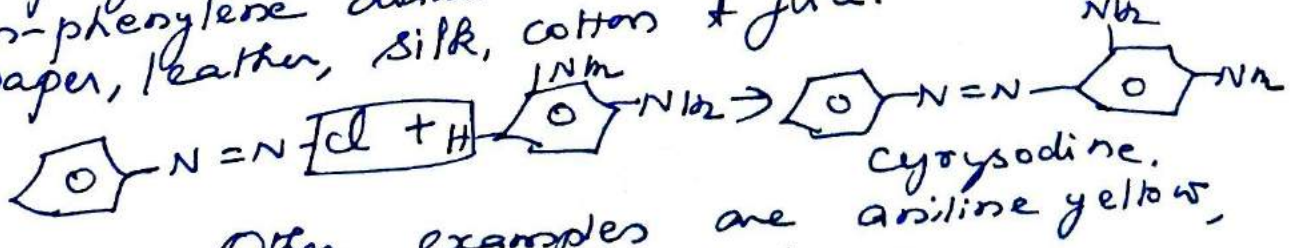


Other examples are fast red, orange G, Naphthol blue, black 6B.

(ii) Cationic dyes / basic azo dyes :-

These dyes have NH_2 / NR_2 groups as the auxochrome. The chromophoric system is present as cation.

(Eg) Cyrysodine which is prepared by coupling benzene diazonium chloride with m-phenylene diamine. It is used for dyeing paper, leather, silk, cotton & jute.



Cyrysodine.

Other examples are aniline yellow, butter yellow & bismark brown.

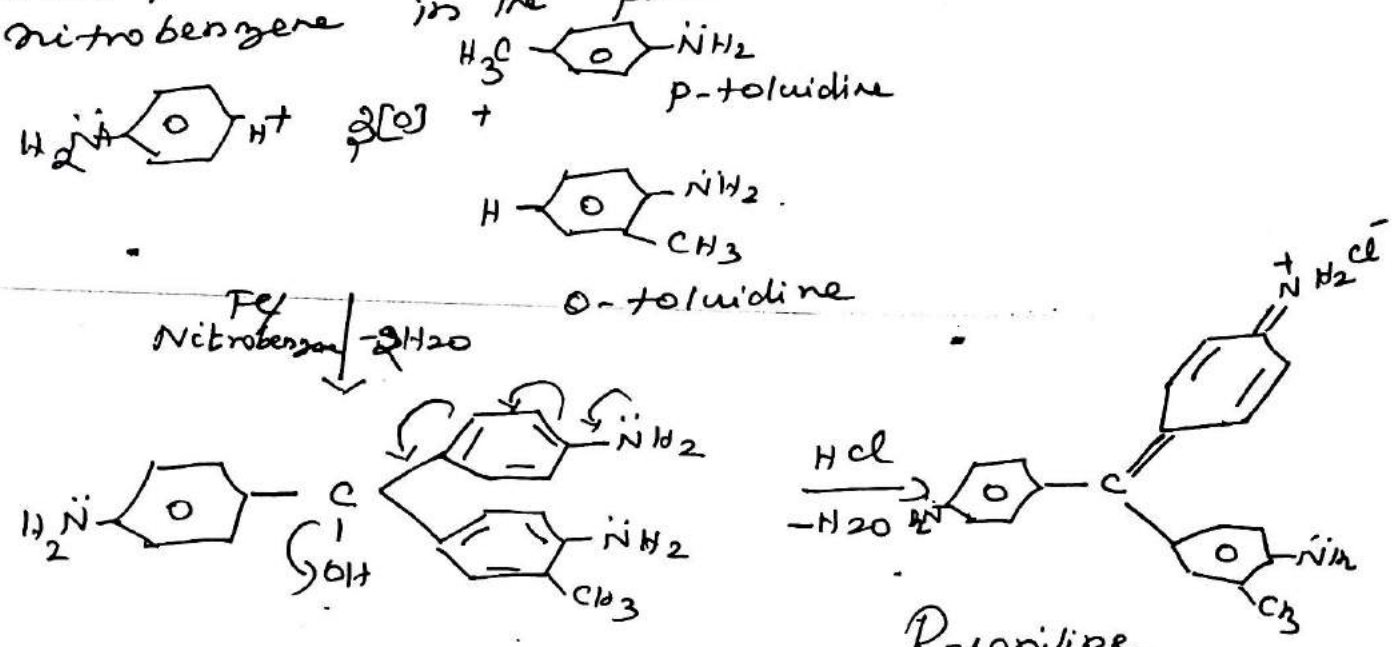
(iii) Mordant dyes :-

These dyes produce fast-wash colours. (Eg) ~~cargoned~~.

ROSANILINE :- (FUCHSINE / MAGNETA)

Preparation:-

It is prepared by the oxidation of equimolecular proportions of aniline, o-toluidine and p-toluidine and their hydrochlorides with nitrobenzene in the presence of iron fillings.



USES:-

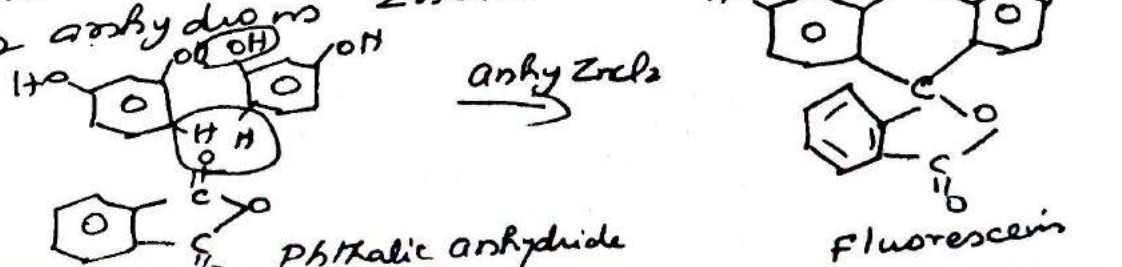
(1) Rosaniline has a greenish metallic lustre. It dissolves in water to give a deep-red colour. It is used for dyeing cotton, silk and wool. Premordanting with tannin is needed for dyeing cotton.

(2) Addition of SO_2 to the dye solution produces the colourless Schiff's reagent which is used to test the presence of aldehydes.

XANTHEN DYES:-

FLUORESCEIN:-

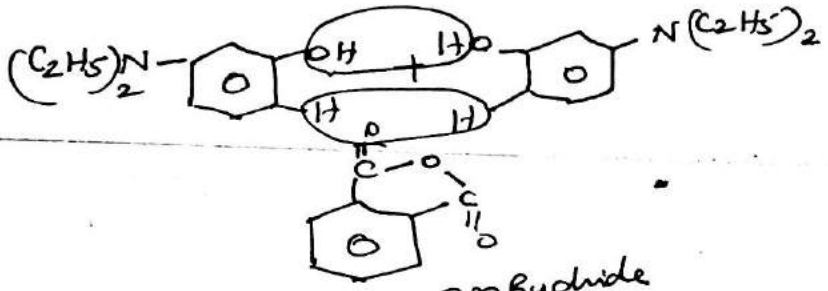
It is a Xanthen dye prepared by condensing two molecules of resorcinol with phthalic anhydride in the presence of conc H_2SO_4 or anhydrous $ZnCl_2$.



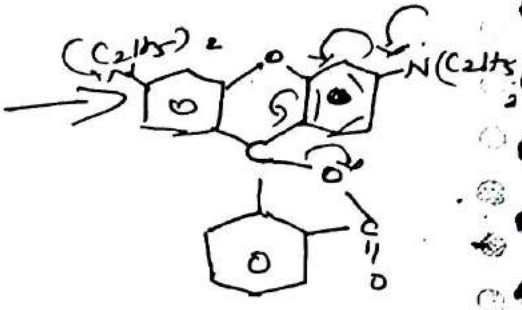
Uses:-
① Sodium salt of fluorescein is known as Uranine and ② Used as a dye for wool & silk
③ Used as a purgative. (for purification)
④ Used for detecting leakage in pipes.
⑤ A dilute solution of fluorescein NaOH gives a green fluorescence when

RHODAMINE B :- Strong yellow-green

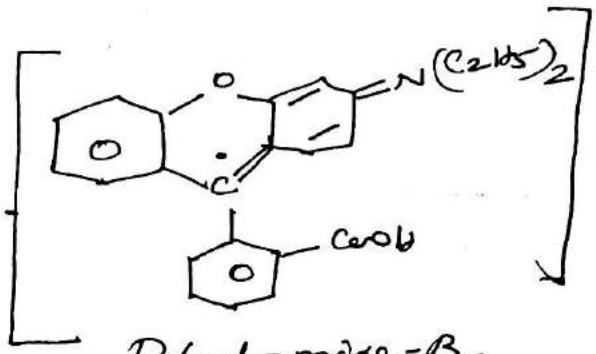
It is prepared by condensing phthalic anhydride with N,N-diethyl-m-aminophenol in the presence of $ZnCl_2$ and treating the product with HCl.



phthalic anhydride



↓ HCl

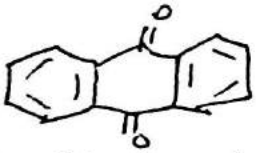


Rhodamine-B.

Uses:-
Rhodamine is used for dyeing silk, wool and cotton.
* exposed to light. It is used to trace pollution of water supplies by sewage, since it a small quantity of it is put in at the suspected source of pollution, the colour will be detectable at some distance from the source, even after extensive dilution.

ANTHRAQUINOID DYES:-

In anthraquinoid dyes, p-quinoid group is fused to two other benzene rings as follows:

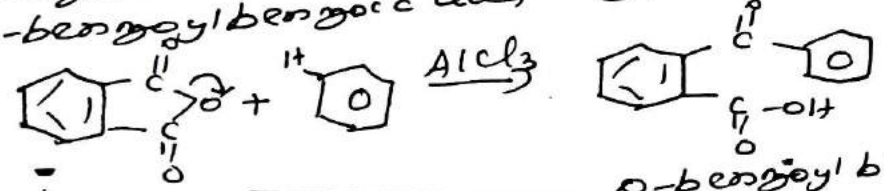


ALIZARIN:-

It is 1,2-dihydroxyanthraquinone

PREPARATION:-

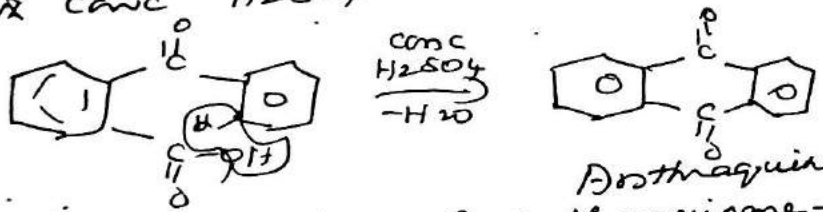
Step I:- Phthalic anhydride is treated with benzene in the presence of $AlCl_3$ to give o-benzoylbenzoic acid (Friedel Crafts Reaction)



o-benzoyl benzoic acid.

Step II:- Formation of anthraquinone:-

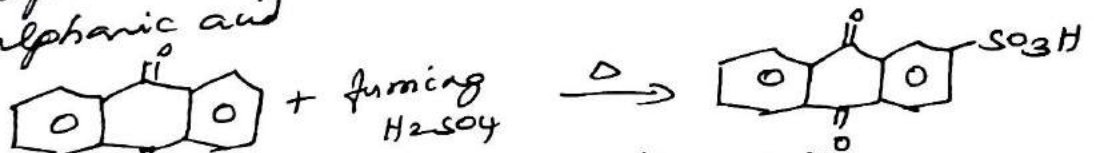
o-benzoylbenzoic acid is cyclized by treatment with conc H_2SO_4 to form anthraquinone.



Anthraquinone.

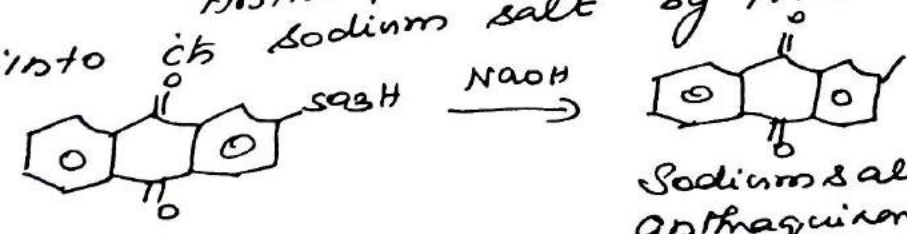
Step III:- Formation of anthraquinone-2-sulphonic acid:-

Anthraquinone is heated with fuming sulphuric acid at 180°C to give anthraquinone-2-sulphonic acid



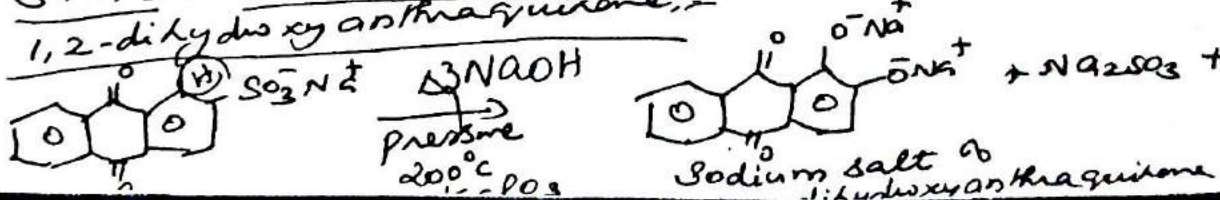
STEP IV:- Conversion into sodium salt:-

Anthraquinone-2-sulphonic acid is converted into its sodium salt by treatment with NaOH.



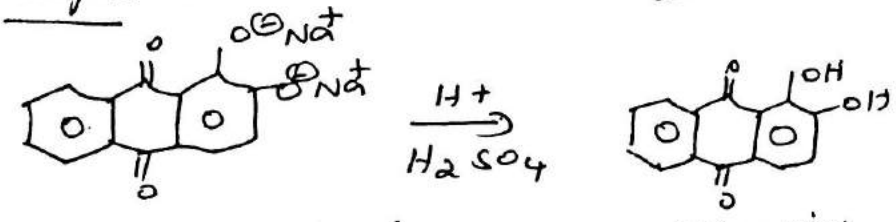
Sodium salt of anthraquinone-2-sulphonic acid

STEP V:- Conversion into sodium salt of 1,2-dihydroxyanthraquinone:-



Sodium salt of 1,2-dihydroxyanthraquinone

Step vi Conversion to alizarin (1,2-dihydroxy anthraquinone)



Alizarin

Sodium salt of 1,2-dihydroxyanthraquinone is treated with Conc H_2SO_4 to give alizarin.

USES:-

① Alizarin is the best known mordant dye. with different mordants, it yields different colours.

(i) with aluminium salt - rose red colour
(ii) with chromium salt - brown violet colour
(iii) with ferric salt - violet black colour
(iv) with barium salt - blue colour.
(v) with magnesium salt - violet colour.

Aluminium & iron lakes are used for dyeing and printing cotton cloth. Aluminium and chromium lakes are used for dyeing wool.

② It is used as a purgative in medicine

③ Its two derivatives alizarin orange and alizarin red are used as dye for wool.

④ It is used in the manufacture of printing inks

⑤ It is used in the preparation of anthrarobin

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