CY8292 _ CFT

UNIT V : COLORANTS

1) (I) Define colour. What are constituents of colour?

(II) Write the synthesis of methyl red.

Constituents of colour

Colour

Colour is a psychological sensation produced when the rays of visible range approach the eye.

White and Black colour :

When white light falls on a substance there are two extremes,

(i) If the bands are totally reflected the substance appears to be white.

(ii) But, if the bands are totally absorbed, the substance appears to be black.

Theory of colour and Constitution

Of many theories, introduced to establish a relationship between Colour and constitution. Witt's theory is an important theory.

O.N. Witt pointed out that all coloured organic compounds contain certain unsaturated groups

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which are responsible for colour, these groups are called as Chromophores.

1) Chromophores (chromo – colour + phoros – bearing)

The presence of one or more unsaturated linkages (π – electrons) in a compound is responsible for the colour of the compounds, these linkages are referred as chromophores.

Chromogen

A compound containing a chromophore is called chromogen. If the chromogen has one or more auxochromes, the resulting substance is called a dye.

Dye = Chromogen + Auxochrome

Examples for chromophores

1.) Ethylene group $\backslash C=C /$

2) Carbonyl group $>C=O$

3.) Azo group $-N=N-$

4.) Nitro group $-NO_2$

5) Nitroso group $-NO$

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(iii) Triketopentanone having three ketonic group is orange.

$CH_3CO\,COCO\,CH_3$

Triketopentanone (orange)

2. Auxochrome (Colour fixing groups)

It refers to an atom or a group of atoms which deepens the colour of a chromogen but cannot by themselves impart colour to a compound.

Examples for auxochrome

1.) Hydroxyl ($-OH$) group

2.) Amino group ($-NH_2$)

3.) Chloro group ($-Cl$)

4) Bromo group ($-Br$)

5) Iodo group ($-I$)

Types of Auxochrome

Auxochrome are of Four types.

1.) Bathochromic groups

Those groups which deepen colour of a chromogen are called bathochromic group. ie., They cause displacement to longer Wavelength.

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Types of Chromophores

There are two types of chromophores

(i) Independant chromophores

A single chromophores is sufficient to impart colour to the compound.

Example:

Azo group ($-N=N-$), nitroso group ($-NO$)

(ii) Dependant Chromophores

More than one chromophore is required to produce colour in the chromogen.

Example:

$>C=O$ group, $>C=C<$ group.

Illustration:

(1) Acetone having one ketonic group is colourless

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

Acetone (colourless)

(ii) Diacetone having two ketonic group is yellow

$CH_3CO\,CO\,CH_3$

Diacetone (yellow)

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ii) Hypsochromic groups

Those groups which lighten the colour of a chromogen are called hypsochromic groups. i.e., they cause displacement to shorter wavelength.

(iii) Hyperchromic effect

Structural changes that increasing the intensity of absorption are said to be hyperchromic effect.

iv) Hypochromic effect.

Structural Changes that decreasing the intensity of absorption are called hypochromic effect.

Illustration

In chloroethylene, $CH_2 = CHCl$,

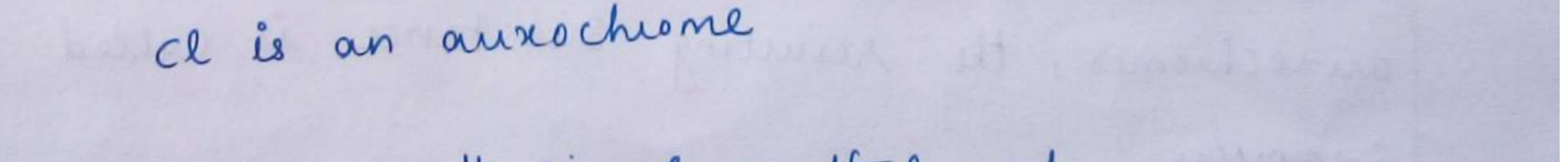
C=C is a chromophore

Cl is an auxochrome

II) Write the synthesis of methyl red

Methyl red is obtained by the coupling of diazotised anthranilic acid with dimethyl aniline.

Methyl red is not used as a dye.



Anthranilic acid Dimethyl aniline Methyl red

Uses

It is used as an indicator in acid alkali titration.

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(2) Explain Witt's theory of colour and constitution with respect to dyes. [Refer, Q.NO. 1]

(3) Support the chromophore and auxochrome theory of, confiam methyl organge and congo red as dyes.

Chromophores

The presence of one or more unsaturated linkages (π-electrons) in a compound is responsible for the colour of the compound, these linkages are refered to as chromophores.

Chromogen

A compound containing a chromophore is called chromogen. If the chromogen has one or more auxochromes, the resulting substance is called a dye.

Examples

1) Ethylene group $>C=C<$

2) Carbonyl group $>C=O$

3) Azo group $-N=N-$

4) Nitro group $-NO_2$

5) Nitroso group $-NO$

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Auxochromes

It refers to an atom or a group of atoms which deepens the colour of a chromogen but cannot by themselves impart colour to a compound.

Examples

1) Hydroxyl $-OH$

2) Amino $-NH_2$

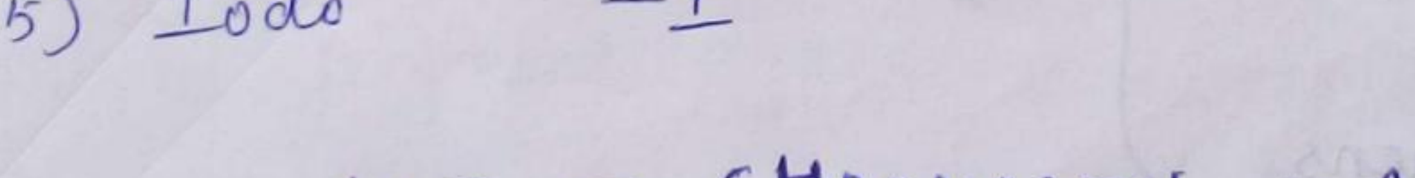
3) Chloro $-Cl$

4) Bromo $-Br$

5) Iodo $-I$

DYE = CHROMOGEN + AUXOCHROME

Methyl orange



Chromophore or Chromogen $\Rightarrow -N=N-$

Auxochrome $\Rightarrow -SO_3H$ and $-N(CH_3)_2$

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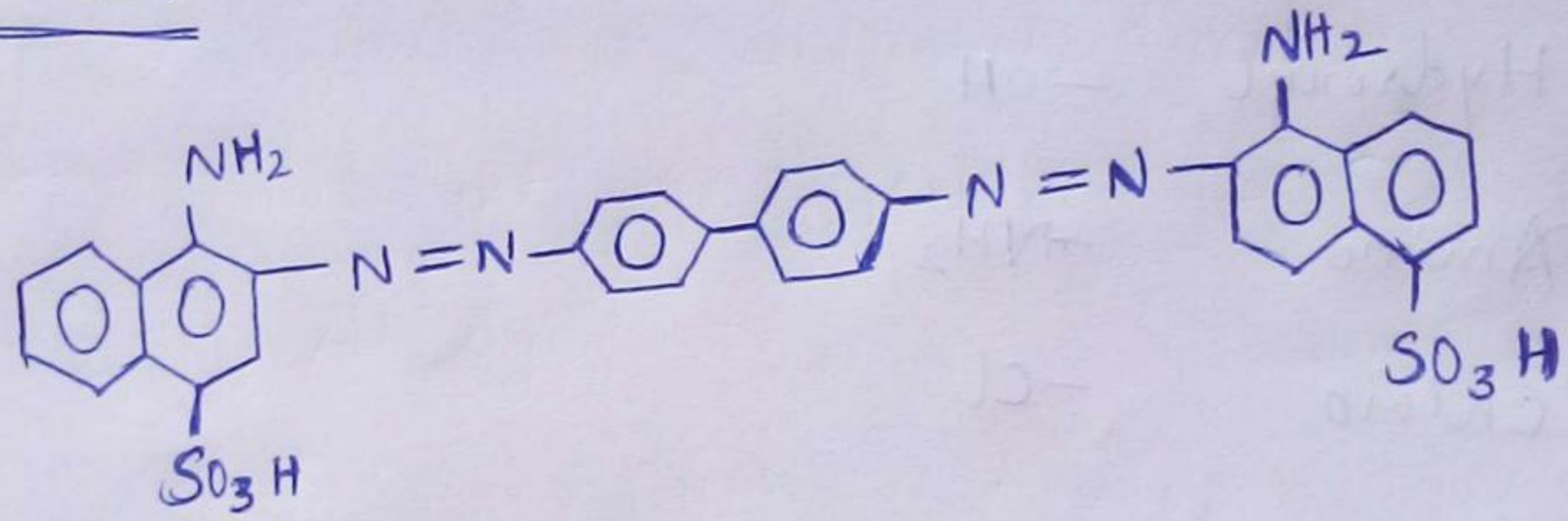
⇒ It is a acid azo dyes are characterised by the presence of one or more acidic groups $-SO_3H$. Their sodium salts are commonly employed for dyeing

⇒ Meltyl orange is prepared by diazotising sulphanilic acid and coupling the diazotised sulphanilic acid with dimethyl aniline.

Congo red



Chromophores (or) Chromogens } ⇒ $-N=N-$

Auxochromes ⇒ $-NH_2$ and $-SO_3H$

⇒ It is a direct azo dyes used directly on cellulose fibres without a Mordant. Acidic and basic dyes are ~~not~~ ~~dyed~~ require mordant for dying cellulose fibres.

⇒ Congo red prepared by diazotising benzidine at both ends, and then coupling the resulting bis-diazo salt with two molecules of naphthionic acid.

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(4) Explain classification of dyes based on applications.

Based on application, dyes are classified into ten types.

(1) Acidic dyes (or) Anionic dyes
(2) Basic dyes
(3) Direct (or) Substantive dyes
(4) Mordant (or) Adjective dyes.
(5) Vat dye
(6) In grain dyes (or) Developed dyes
(7) Sulphur dyes
(8) pigment dyes
(9) Solvent (or) Spirit Soluble dyes
(10) Food dyes

(1) Acidic dyes (or) Anionic dyes:

Acidic dyes are the sodium salts of sulphonic acid or phenolic compounds. The colour of the dye is due to the presence of its negative ion. Such anionic dyes are attached to the positively charged amine groups in the fibre.

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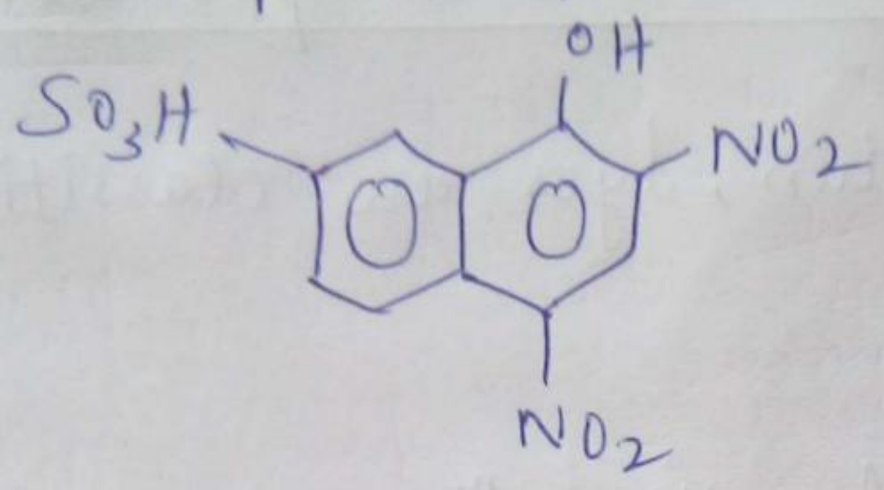
Example

Naphthol yellow S



Process

Fabric, to be dyed, is stirred in hot solution of the dyes in presence and either an acid or salt till it is uniformly dyed. Then it is removed and dried.

Uses

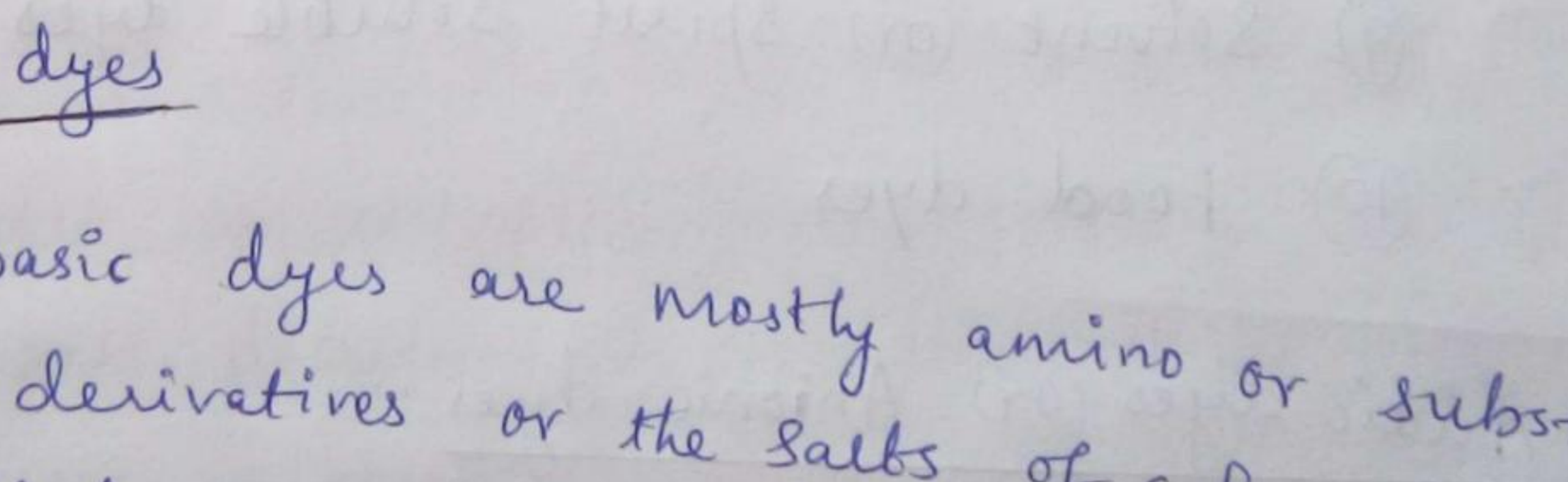
It is used to colour synthetic and natural polyamide fibres like wool, natural silk, etc.

② Basic dyes

Basic dyes are mostly amino or substituted amino derivatives or the salts of coloured bases with HCl or $ZnCl_2$. The colour of the dye is due to the presence of its positive ion.

Example

Methyl violet



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Process

Animal fibres are dyed with basic dyes directly as acidic dyes. but, vegetable fibres (Cotton) must be mordanated. Cotton is first mordanated with tannic or fatty acid salt of alumina. The colour is then developed by heating the mordanated cotton in a bath of basic dyes at about 60°C.

Uses

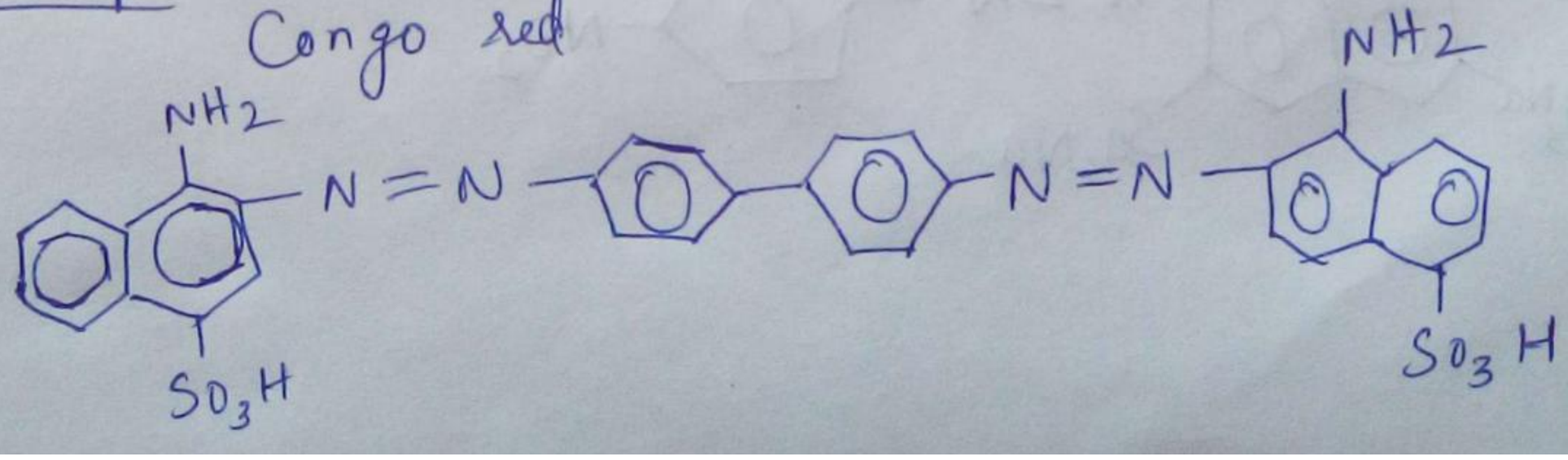
It is applied to paper, Cotton, Silk, etc.

3) Direct (or) Substantive dyes

Substantive dyes are substances of high molecular weight showing colloidal properties and become fixed on the fibre by hydrogen bonding. These dyes are also called salt dyes, because during dying common salt is added to the dye bath. addition of common salt decreases the solubility of the dye and hence causes exhaustion of it from the dyeing solution.

Example:

Congo red



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process

Dye is applied to the fabric, to be dyed, by immersing the fabric in ~~boot~~ hot boiling solution and then removing and dying the fibre.

uses

Direct dyes are used to dye animal and vegetable fibres directly.

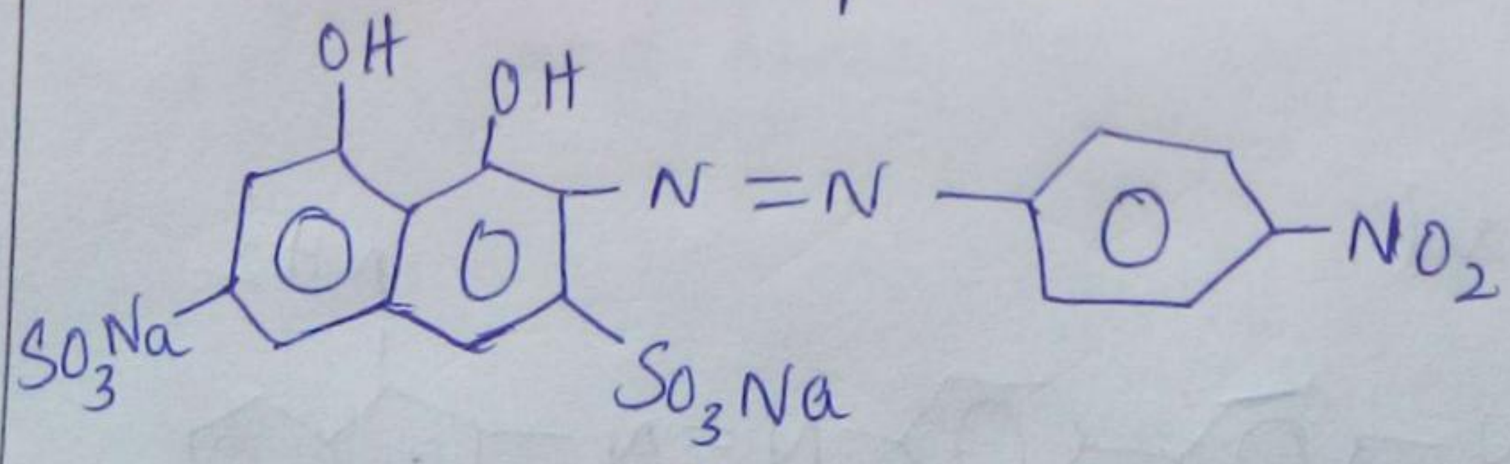
④ Mordant (or) adjective dyes

⇒ These dyes cannot dye animal and vegetable fibres directly. but require the presence of a mordant. The processing agent between cloth and dye is called a mordant. If the dye is acidic in nature, the mordant must be basic and vice-versa.

⇒ The mordant dyeing is really a metallic salt or lake formed in the fibre.

example

Chromotrope 2B



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Process

The colloidal metal hydroxide adheres to the fibre and the dye molecule combines with the metallic mordant to form a complex salt or lake by means of chelation. The lake thus formed is fast to washing.

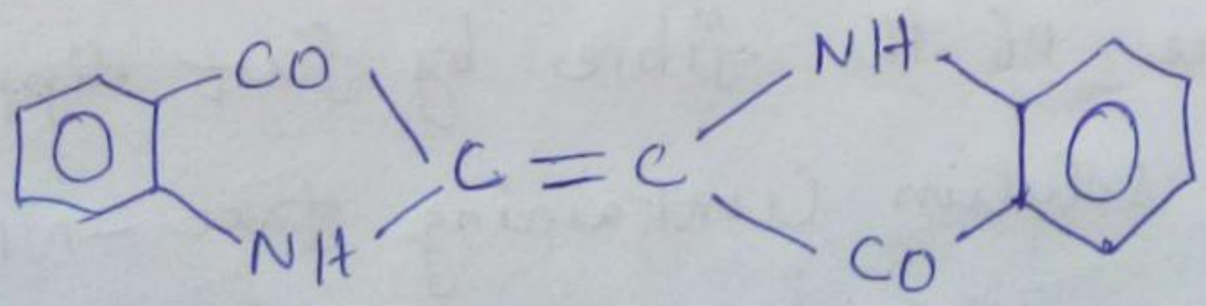
Cotton fibre $\xrightarrow[\text{in mordant}]{\text{Soaked}}$ Mordanted fibre $\xrightarrow{\text{Direct dye}}$ Dyed fibre

⑤ Vat dye

⇒ These dyes are insoluble in water, but their reduced form is soluble in an alkali solution and as a result leuco vat is obtained. If fabric is immersed in the alkaline solution of reduced dye (vat), the leuco compound is adsorbed and when exposed to the air it is oxidised to the dye, which remains fixed to the cloth.

⇒ The process of reduction and solubilization is known as vatting. The reduced compound is white in colour and hence are called leucobase

Ex:



Indigotin

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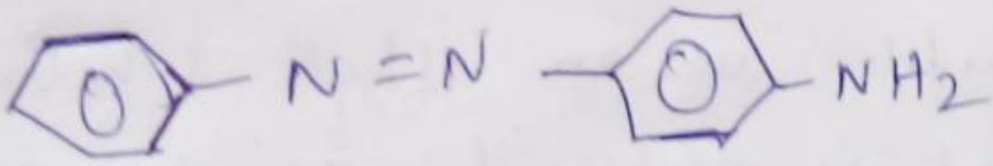
6) In grain dyes (or) Developed dyes

These dyes are produced within the fabric. usually the last stage in the production of these dyes is carried out on the fibre. In grain dyes are classified into three groups.

(a) Ice colours

Since diazotisation and coupling reactions are carried out at low temperature, it is called ice colour.

Example: Aniline yellow (p-aminoazo benzene)



Process

Coupling takes place on the surface of fibre by soaking it first in the alkaline β-naphthol solution and then dipping in ice cooled diazotised solution of p-nitro aniline.

b) Diazotisation

In this techniques, the diazotisation is carried out on the surface of the fibre by first dipping the fibre in dye solution (containing free $-NH_2$ group) and then diazotising this amino group by dipping

it into ice cooled nitrous acid solution followed by immersing the diazotised fibre into a solution of secondary component.

(c) Oxidation

In addition to diazotisation, some other reactions, like oxidation may also be carried out with in the fibre.

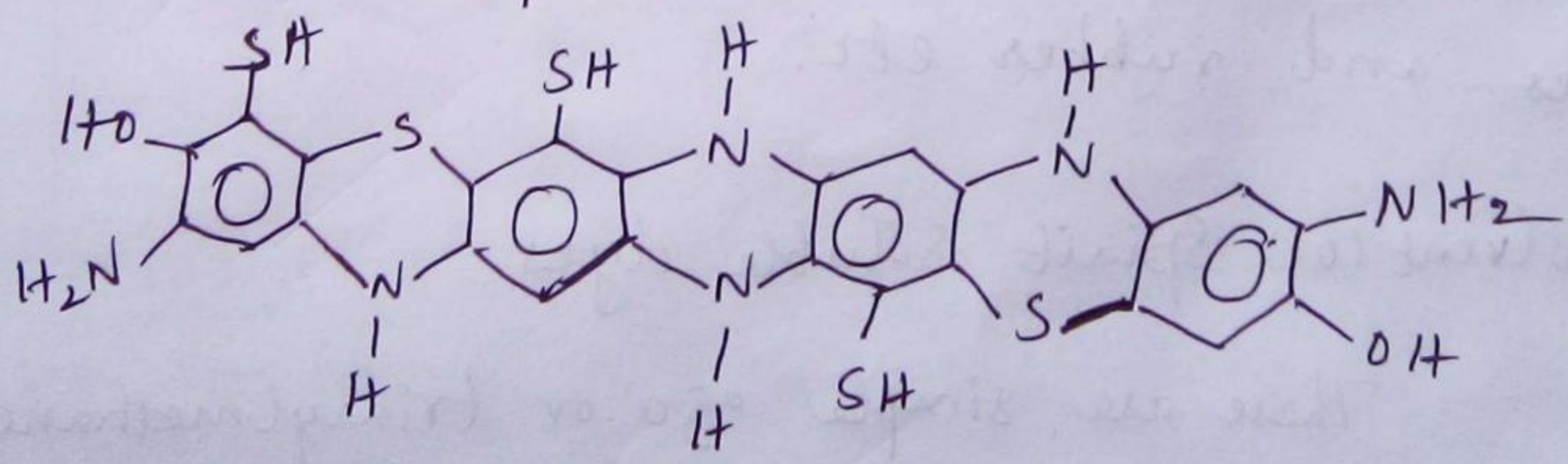
Uses

It is produced on cotton.

F) Sulphur dyes

These are complex substances containing sulphur, which are insoluble in water, but soluble in cold alkaline solution of sodium sulphide (Na_2S), where it is reduced to colourless leuco compound.

Example Sulphur Black



Process

The cotton fibre is dipped in the sodium sulphide solution of the dye and then oxidised

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by exposing to air which oxidises the leuco compound to insoluble dye.

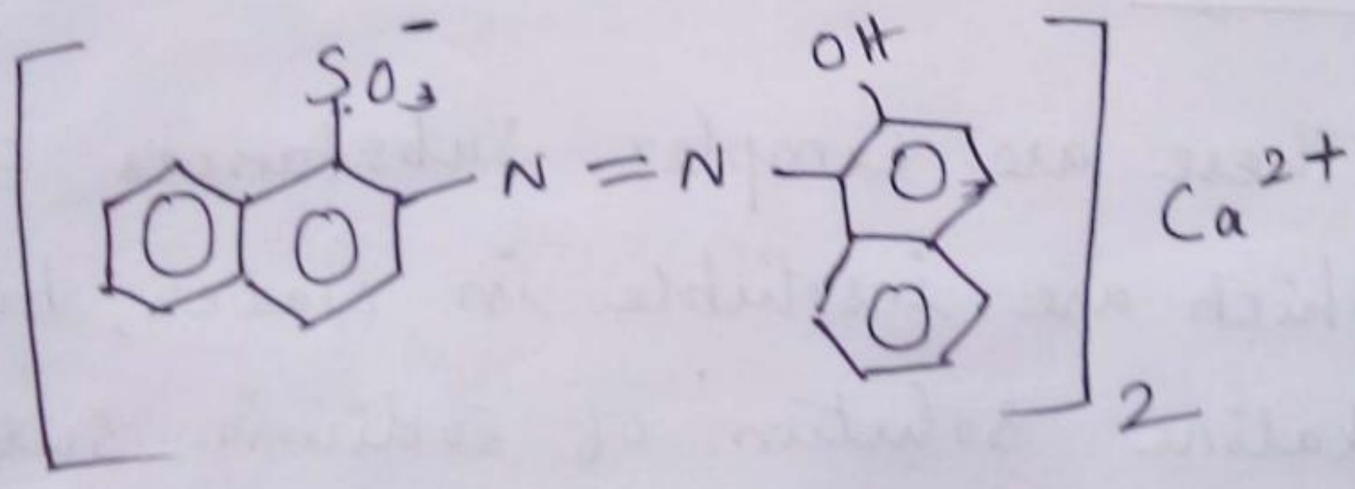
Uses

It is applied on cotton.

⑧ Pigment dyes

These dye molecules contain $-OH$ and $-SO_3H$ groups. They form insoluble compounds (or) lakes with salts of Ca, Cr, Ba and Al.

Example Litthol red.



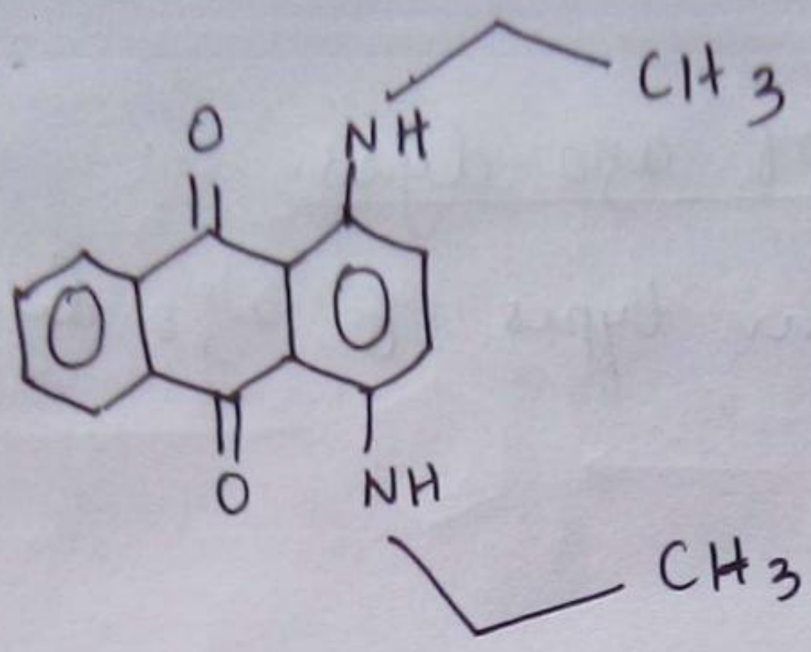
Uses

Used in paints, printing inks, synthetic plastics, fibres and rubber etc.

⑨ Solvent (or) Spirit soluble dyes

These are simple azo or triarylmethane bases.

Example



Uses

It is used to colour oils, waxes, varnishes, gasoline, etc.

(10) Food dyes

These are selected and tested for harmlessness.

Example

Uses:

It is used in Colouring-foods, candles, cosmetics and confectionaries.

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(5) Explain various types of azo dyes.

There are four types of azo dyes

1) Acid azo dyes
2) Basic azo dyes
3) Direct (or) Substantive azo dyes
4) Mordant azo dyes.

1) Acid azo dyes

The acid azo dyes are characterised by the presence of one or more acidic groups $-SO_3H$, $-COOH$ and $-OH$. Their Sodium salts are commonly employed for dyeing.

Examples

Methyl orange, methyl red

(a) Methyl orange

Methyl orange is prepared by diazotising sulphanilic acid and coupling the diazotised sulphanilic acid with dimethyl aniline.

Step1 Diazotisation

Sulphanilic acid is prepared by heating aniline with Con. H_2SO_4. It is then treated

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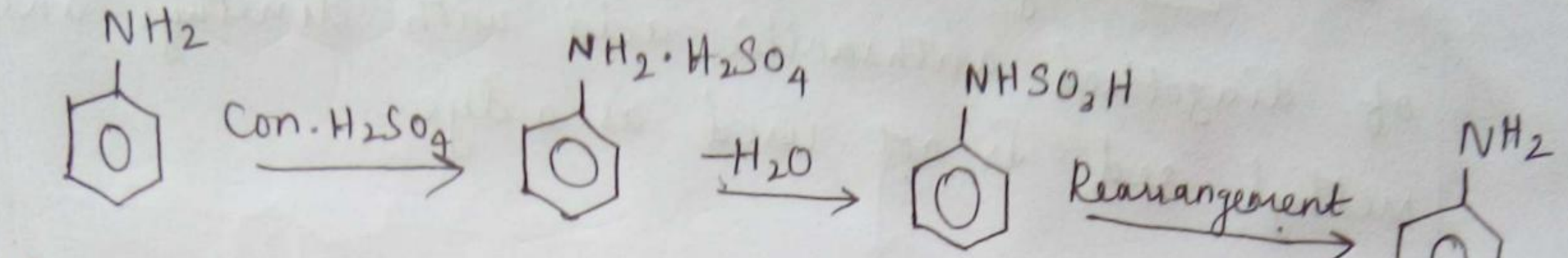
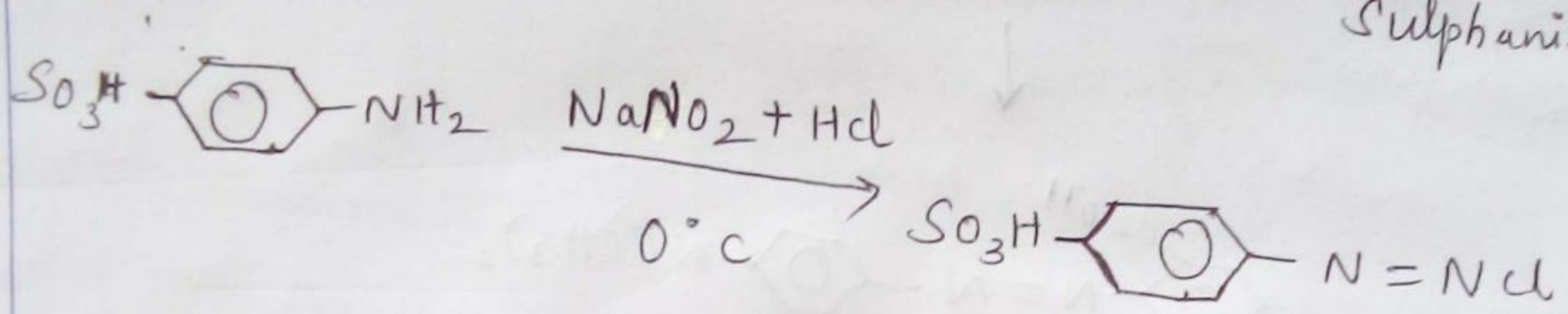
with aqueous sodium nitrate at 5°c to get diazotised sulphanilic acid.



Aniline

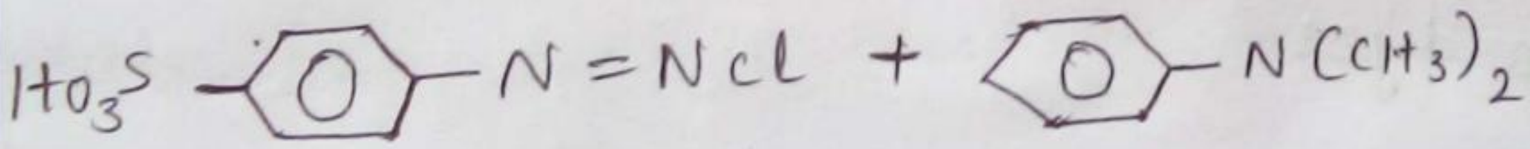
Sulphanilic acid



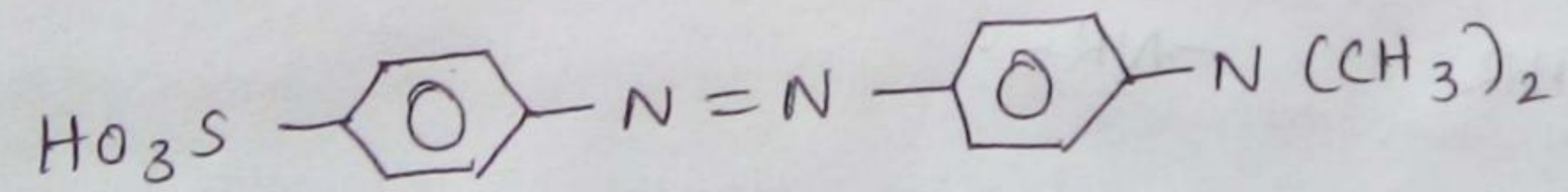
Diazotised sulphanilic acid.

Step II Coupling reaction

The diazotised sulphanilic acid is allowed to react with dimethylaniline to give methyl orange.



Dimethyl. aniline



Methyl orange

Uses

It is used as an indicator.

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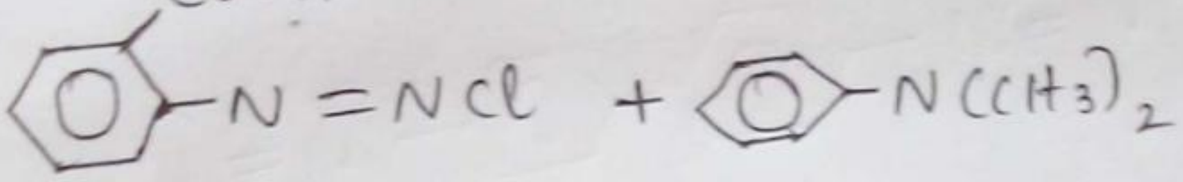
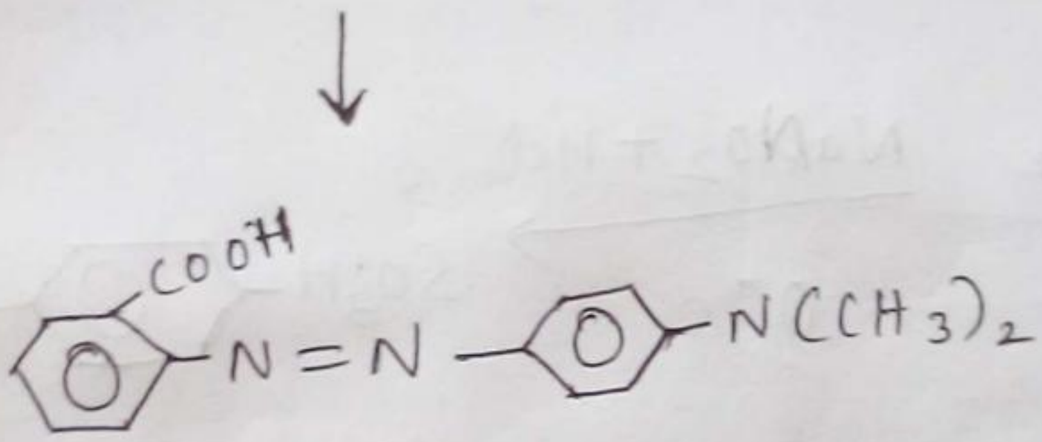
b) Methyl red

Methyl red is obtained by the coupling of diazotised anthranilic acid with dimethyl aniline. Methyl red is not used as a dye.





Methyl red

Uses

It is used as an indicator in acid alkali titration.

2) Basic azo dyes

The basic azo dyes are characterized by the presence of amino or substituted amino groups $-NH_2$, $-NHR$ or $-NR_2$.

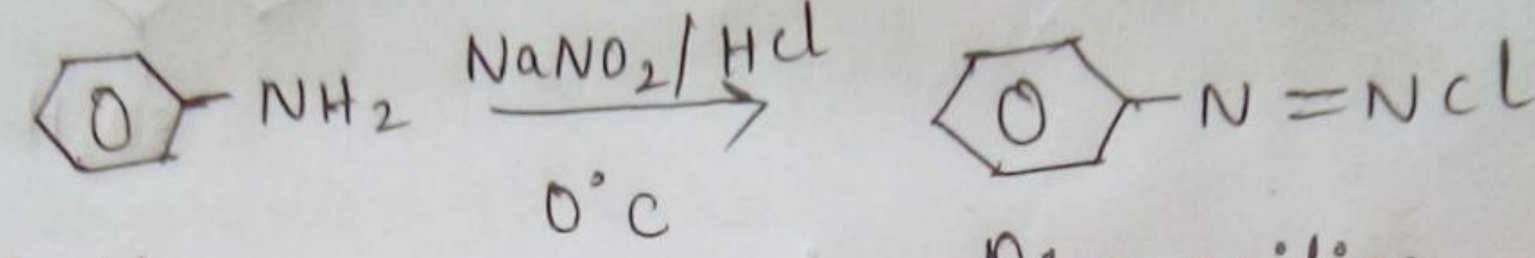
Example:

Aniline yellow, Bismarck brown, etc.

Aniline yellow

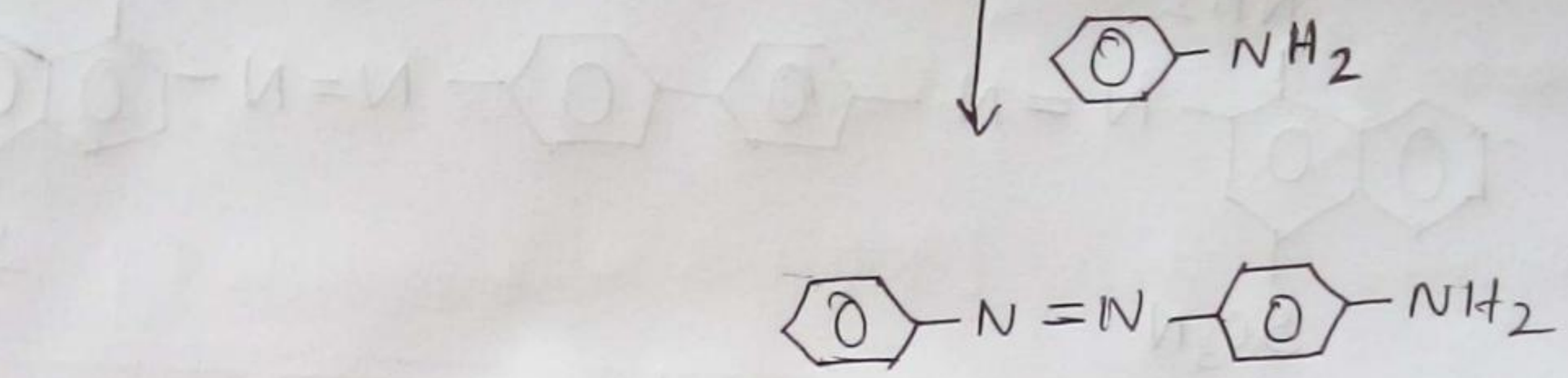
It is prepared by coupling of diazotised

aniline with aniline.



Aniline

Diazo aniline



Aniline yellow

(p-aminoazo benzene)

3) Direct (or) Substantive dyes

Direct azo dyes are used directly on cellulose fibres without a mordant. But acidic and basic azo dyes are dyed directly the proteinous fibres but require mordant for dying cellulose fibres.

Example Congo red

Congo red

It is prepared by diazotising benzidine at both ends, and then coupling the resulting bi-diazo salt with two molecules of naphthionic acid.

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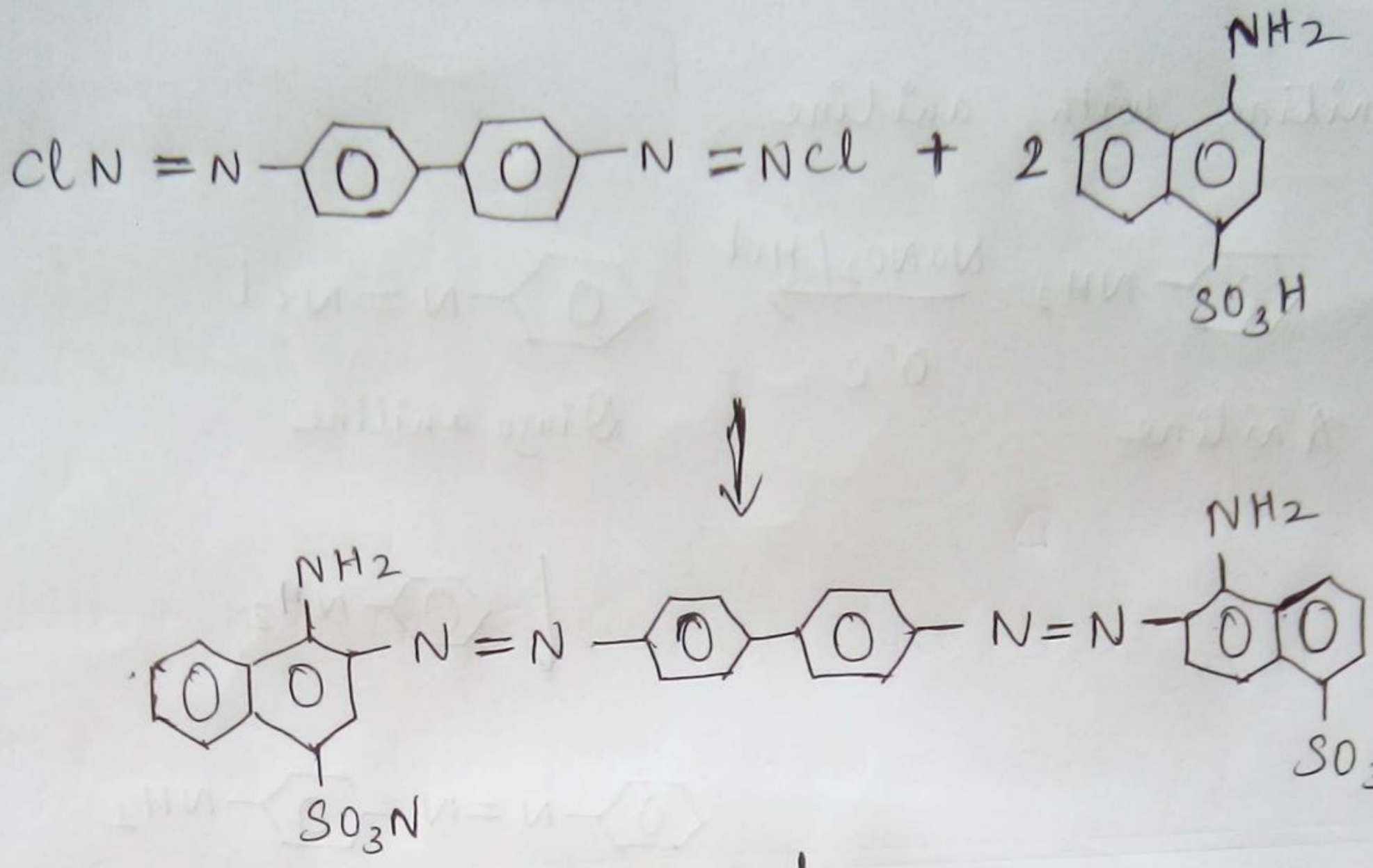


Congo red

Congo red

It is prepared by diazotising benzidine at both ends and then coupling the resulting bis-diazo salt with two molecules of naphthionic acid.

4) Mordant azo dyes

These dyes form compleres with mordants such as oxides of chromium, cobalt, copper, aluminium etc.. Chromium is the most widely used metal in mordant dyes. Such dye is known as azochrome mordant dye.

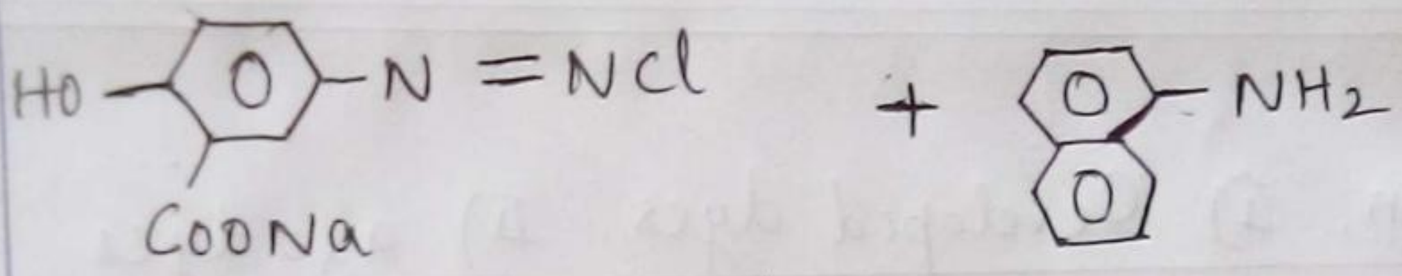
Examples

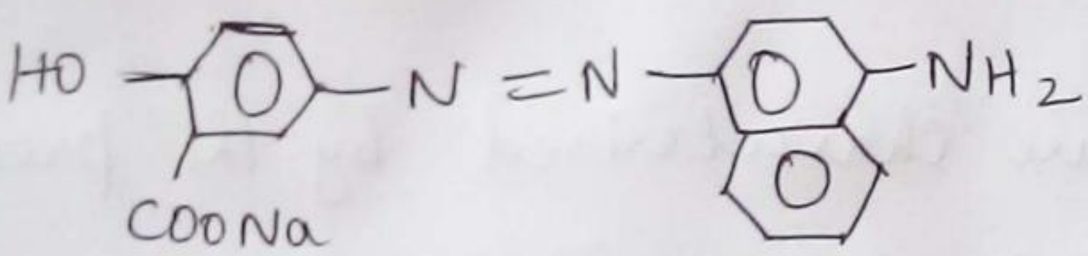
Carmoisine, diamond Black F, Chromotrope 2B, etc.

Diamond Black F

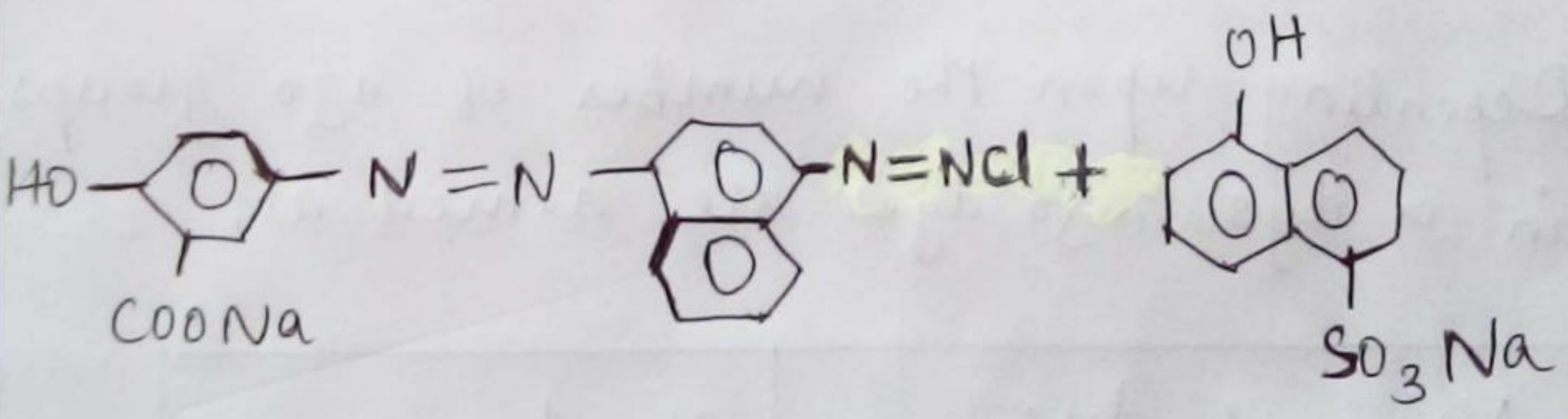
It is an important mordant dye. It is

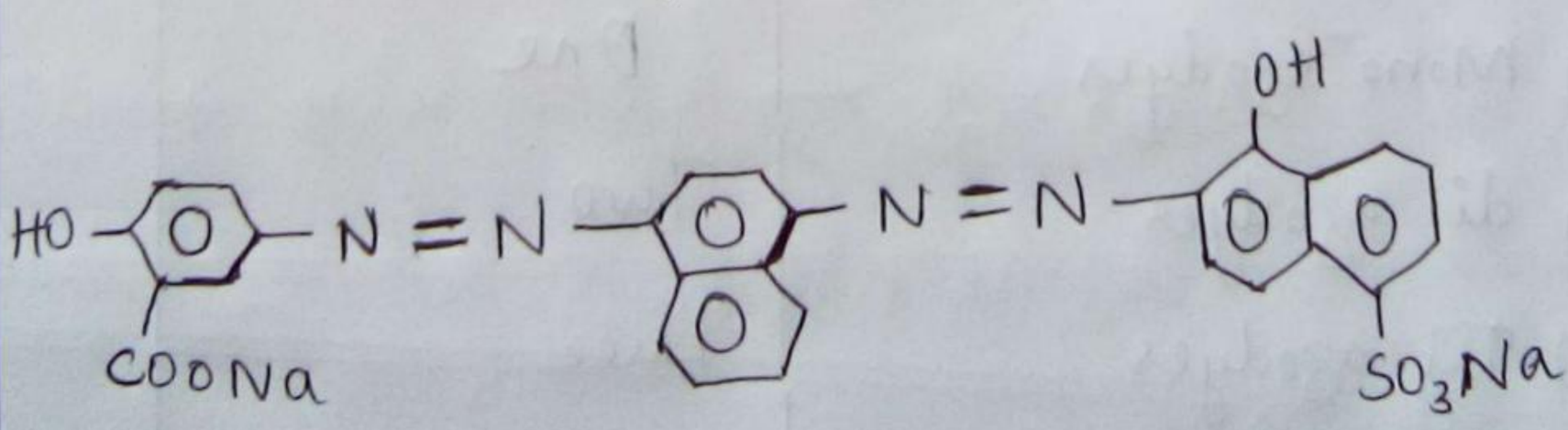
prepared by coupling of 5-amino Salicylic acid with 1-naphthylamine and amino Azo dye thus formed is diazotised and coupled with 1-naphthol-4 or 5-Sulphonic acid.





$NaNO_2$
HCl





Diamond Black F

Uses:

1) Chromium compleres are suitable for wool

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and silk.

2) Copper complexes are suitable for cellulose fibre.

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(6) Write a note on, I) Developed dyes, II) azo dyes

I) Developed dyes [Refer Q. NO. 4, subtitle 6]

II) Azo dyes

All azo dyes are characterised by the presence of azo groups (−N=N−) as chromophore.

Naming

Depending upon the number of azo groups present in a dye, azo dyes are named as,

Name of dye	Number of azo groups present
1) Mono azodyes	One
2) di azodyes	Two
3) Tri azodyes	Three
4) Tetra kisazo dyes	Four

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Synthesis

Azo dyes are prepared in two steps.

Step I Diazotisation

Diazotisation may be carried out by dissolving aniline in dil. HCl and then adding slowly the aqueous solution of sodium nitrite at 5°C.

$$RNH_2 + HNO_2 + HCl \longrightarrow R-N_2^+Cl^- + 2H_2O$$

Diazonium chloride

Step II Coupling reaction

The reaction between a diazonium salt and a phenol giving hydroxy-azo compound is known as coupling. It is carried out between 0°C and 10°C.

$$R-N_2^+Cl^- + HR'OH \longrightarrow RN=NR'OH + HCl$$

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(7) Write a note on, I) Acidic dyes

II) Basic dyes

III) Mordant dyes

[Refer Q.NO.4, Subtitle 1, 2, 4]