Q Discuss the factors which are responsible for complications in IR spectrum.

Ans → Following are the factors which are responsible for complications in IR spectrum.

1. Overtones

2. Combination bands — When two fundamental bands absorbing + $\bar{\nu}_1$ and $\bar{\nu}_2$ absorb energy simultaneously.

3. Fermi resonance → When an overtone or combination band has same frequency as fundamental band. Here two bands appear splitted on either side of the expected value and have same intensity. These two are called Fermi doublets and Phenomenon is called Fermi resonance.

4. Hydrogen bond formation, dipole interaction or intermolecular interaction may shift a band or broaden them.

5. In finger print region, banding and skeletal vibration are difficult to assign because steric effect or electromeric effect lead to large shift.

Q. What is Fermi resonance? Explain taking suitable examples. 13

Ans → In IR Spectrum, absorption bands are spread over a wide range of frequencies. Hence, there may have a chance that energy of an overtone level may coincide with the fundamental mode of different vibrations. As a result, a type of resonance occurs which occurs in case of coupled pendulum. This is called Fermi Resonance.

Here it may be explained in such a way that a molecule transfers its energy from fundamental band to overtone and back again. According to the quantum mechanics, resonance pushes the two levels apart and mixes their character so that each level becomes partly fundamental and party overtone in character. Hence, this resonance gives rise to a pair of transitions of equal intensity.

Let us take the example of CO_2 molecule.

Total no of fundamental vibrations $= 3N-5$
$= 3\times3-5$
$= 9-5$
$= 4$

out of four

① Stretching (Symmetric) $\overleftarrow{O}=C=\overrightarrow{O}$ IR inactive because $\mu=$

② Stretching (Asymmetric) $O\overrightarrow{=}C\overrightarrow{=}O$ IR active

③ 2 Bending vibrations of same energies
a) In the plane IR active
b) Out of the plane IR active

stretching (symmetry) is Raman active and shows a strong band at 1337 cm^{-1}

The two bending vibrations are equivalent and absorb at same frequency 667.3 cm^{-1}.

Now, its overtone becomes $2 \times 667.3 = 1334.6$ cm^{-1}

This value (1334.6 cm^{-1}) is very close to 1337 cm^{-1} (Raman active symmetric stretching vibration).

Hence, here Fermi Resonance takes place

The mutual perturbation of Fundamental (1337 cm^{-1}) and overtone (1334.6 cm^{-1}) gives rise to two bands at 1285.5 cm^{-1} and 1388.3 cm^{-1} having the intensity ratio of 1 : 0.9

Similarly, Fermi Resonance is given by aldehydes in which C—H stretching absorption gives a doublet ~2820 cm^{-1} and ~2720 cm^{-1} due to perturbation between C—H fundamental stretching and overtone of C—H bending

Also, acid anhydride show two C=O stretching absorption between 1850–1800 cm^{-1} and 1790 – 1745 cm^{-1}

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Q What do you understand by the term dye? What are the requisit conditions for a substance to behave as a dye.

Ans → A dye may be defined as coloured substance which can be applied in solution or in dispersion on a surface like cotton, wool, silk, polyester, paper, leather, hair, plastic, cosmetic base to give a coloured appearance.

Following conditions must be satisfied to become a dye :-

a) It must have suitable colour.

b) It must be able to be fixed on a surface from solution state.

c) It must be fast to light & heat.

d) It must not be affected by water

e) It must not be affected by organic solvents

f) It must resistant to action of soap and detergent.

Q. Discuss classification of Dye

Ans → Dyes may be classified in a number of ways. Some of these are as follows:—

(A) On the basis of occurrence in nature →

i) Natural dyes → These are obtained from nature eg indigo and alizarine

ii) Artificial dyes → These are prepared artificially. Most of the artificial dyes are prepared from Coal-tar. Hence, these are called as coal-tar dyes.

(B) On the basis of their chemical constitution →

Dyes may also be classified on the basis of the functional group which impart colour. Important classes on this basis are

i) AZO dyes
ii) Nitro dyes
iii) Nitroso dyes
iv) Triphenylmethane dyes
v) Anthraquinone dyes
vi) Phthalein dyes etc.

(C) On the basis of their applications →

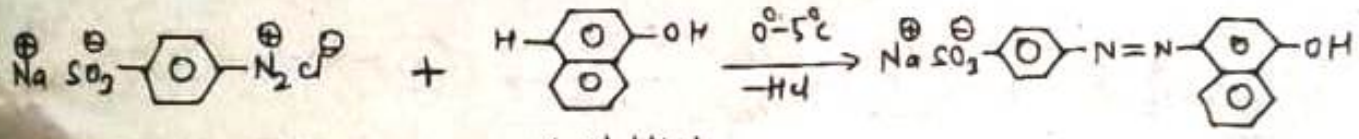
The application of a dye on a particular fibre depend upon the nature of fibre as well as nature of dye. dyes are attached on the fibre with the help of covalent, ionic or hydrogen bond as well as by van der Waals force. These are of following types:

1) Acid dyes → These dyes are applied on the fibre from their acid solutions. They are used to dye wool, silk, nylon etc. fibres. These dyes contain sulphonic acid group ($-SO_3H$) and carboxylic acid group ($-COOH$). eg sodium salt of azo dyes containing these groups.

This is a better dye for nylons because they contain higher proportion of amino group. This is not a good dye for cotton fibre.

eg Orange I, Orange II, methyl Orange, congo red etc.

Preparation of Orange I

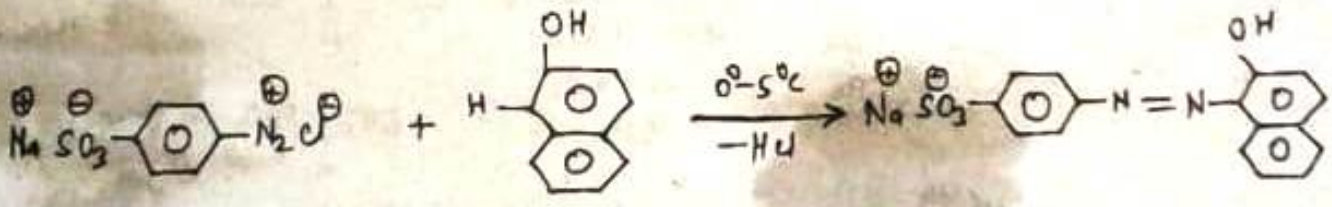


Sodium salt of diazotised Sulphanilic acid

α-Naphthol

Orange -I

Preparation of Orange -II



β-naphthol

Orange -II

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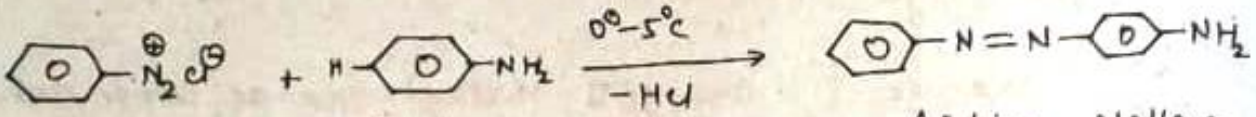
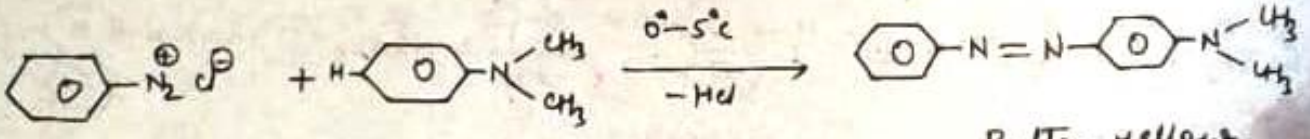
ii) Basic dyes → These dyes are salts of coloured bases containing amino gr ($-NH_2$) or alkyl substituted amine grp ($-NR_2$). $-NH_2$ group or $-NR_2$ group act as auxochromes. Nylon (modified) and polyester fibre can be dyed with these dyes. This class includes aniline yellow, malachite green, butter yellow, chrysodine G. etc.

Preparation of aniline yellow and butter yellow →

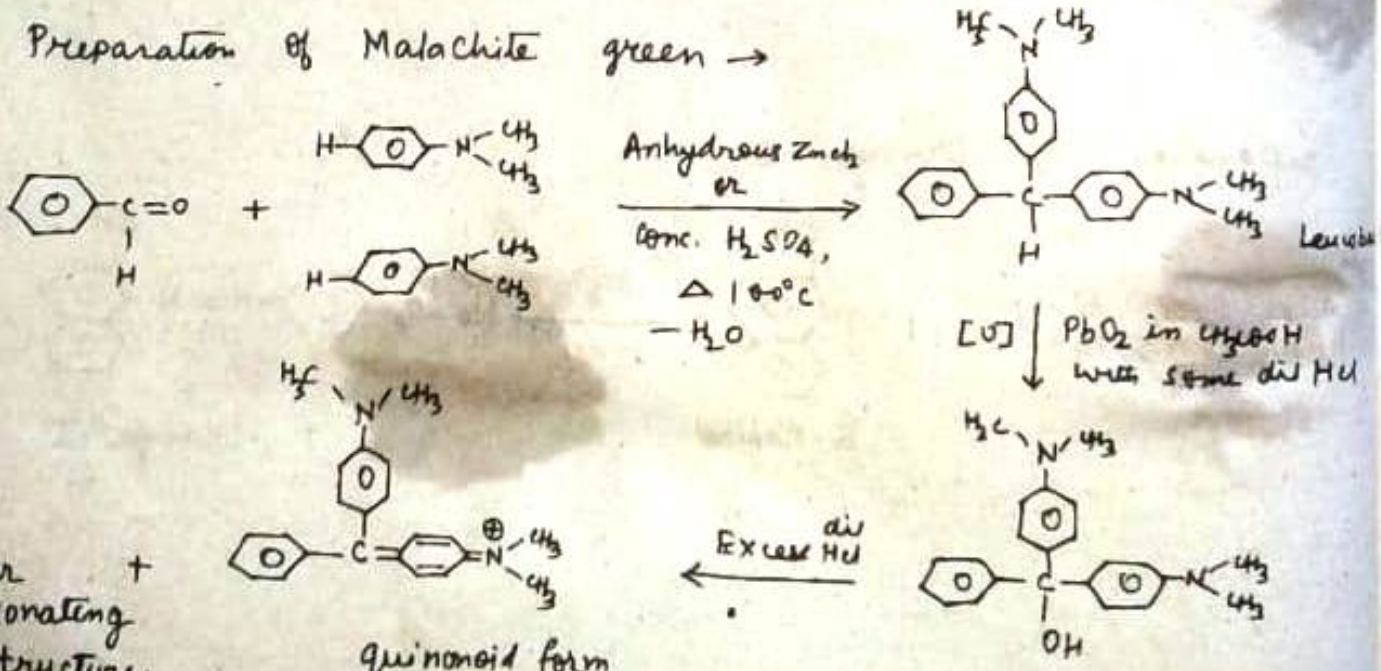


Benzene diazonium chloride + Aniline → Aniline yellow



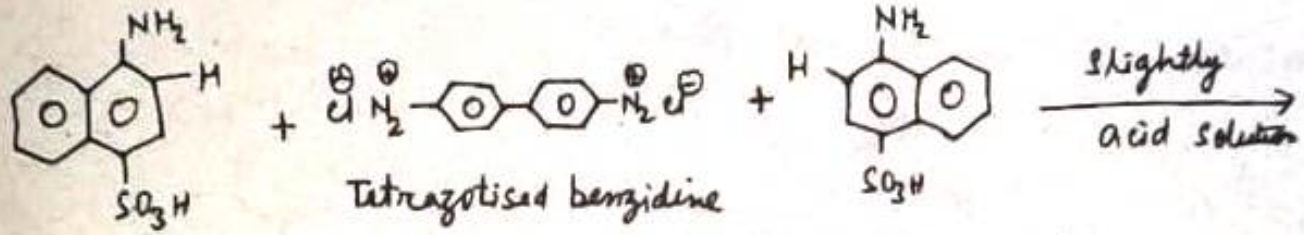
N,N-Dimethyl aniline → Butter yellow

Preparation of Malachite green →



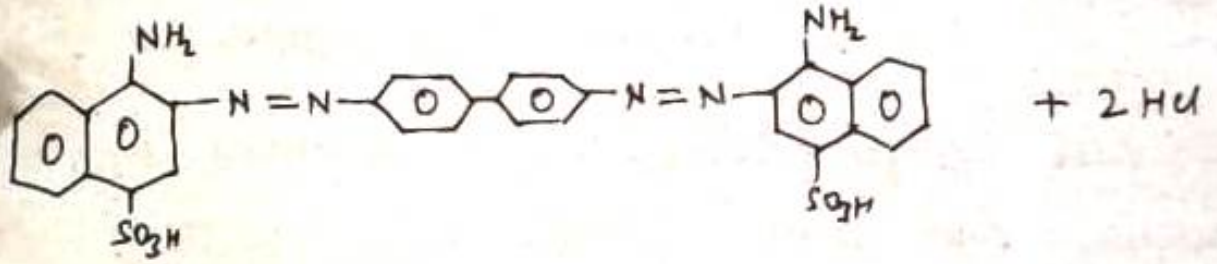
iii) Direct dyes → As the name says, it is water soluble and can be applied to the fabric directly from its aqueous solution. This is most suitable for those fabrics where hydrogen bonds are formed with the dye. eg Congo red and martius yellow.

Preparation of Congo red →



Naphthionic acid

Naphthionic acid



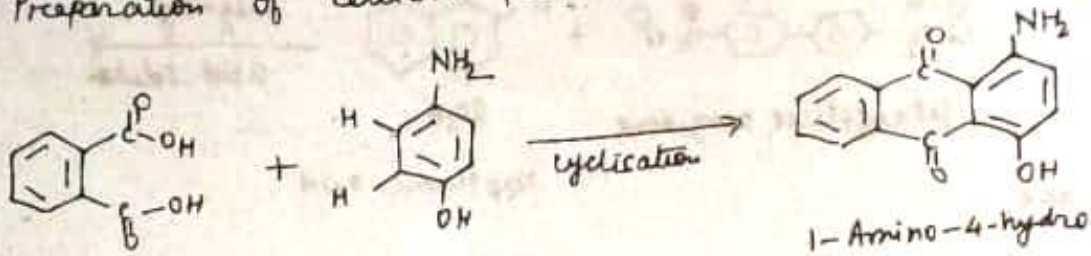
Congo red.

It is not a good dye for textile because colour changes when acid is added. It is mainly used for dyeing paper. Colour develops due to resonance

20.

iv) Disperse dyes → Disperse dyes are insoluble in water and are applied to the fabric in the form of dispercion in a soap solution in presence of some stabilizing agents like, phenol, cresol, benzoic acid etc. These are used to dye synthetic fibre such as nylon, polyester etc.
These dyes belong to the class of anthraquinone dye. eg Celliton fast pink B, Celliton fast blue B.

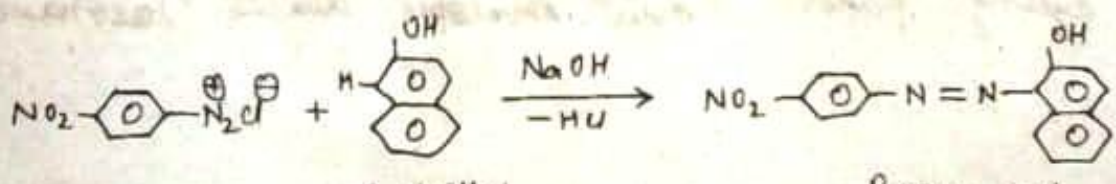
Preparation of Celliton fast pink B.



Phthalic acid | 1-Amino-4-hydroxy Benzene | 1-Amino-4-hydroxy anthraquinone

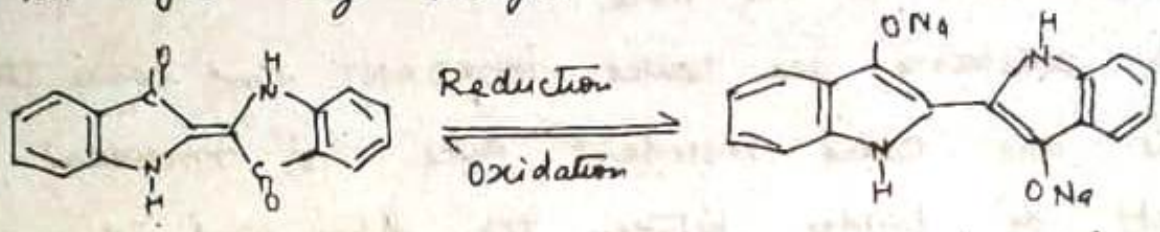
Celliton fast pink B.

v) Insoluble azodyes (Ingrain dyes) → About 60% of available dyes come in this class.
They are obtained by coupling phenols, naphthols, aminophenols adsorbed on the surface of the fabric with diazonium salt. The colour of the dye is not so fast and can be used for dyeing Cellulose, silk, polyester etc. eg para red.



β-Naphthol | Para-red

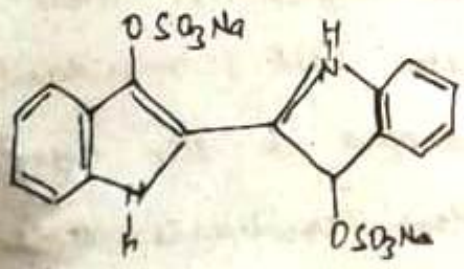
vi) Vat dyes → These dyes are also insoluble in water and can not be used directly for dyeing. Hence, they are converted into soluble form by reduction with reducing agent like alkaline solution of sodium hydrosulphite. This soluble form is called Leucoform. Now, Leucoform can attach with the Cellulose fibre. Hence, this most suitable for Cotton fibre. Entire process is done in a large wooden Container ~~known~~ called as Vats, hence, it is called as vat dyes. eg Indigo.



Indigo

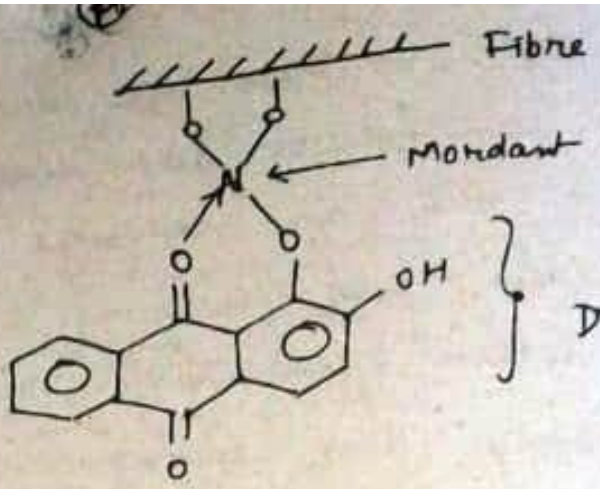
Leucoform.

However, Indigosol O is soluble in water. It is most suitable for wool.



Indigosol O.

VII) Mordant dyes →



Alizarine–aluminium fibre complex
(rose red lake)

These dyes are reluctant to attach with the fibre directly. They require such a chemical substance by the help of which dye can be attached on the fibre. Such substance are called MORDANT. and hence these dyes are called mordant dyes. ie mordant acts as bridge between the fibre and dye

For acid dyes, metal ions are used as mordant but for baric dyes, tannic acid is used as mordant. They are mostly used by wool.

The fabric which is to be dyed is first soaked in the solution of suitable metal salt (mordant) and then soaked fibre is dipped in the dye solution. As a result an insoluble colour complexes are formed called as Lakes.

The same dye can give different colours depending upon the metal ion used.

eg with Al^{3+} ion, alizarine gives rose red (turkey red)
with Ba^{++} ion, blue colour, with Cr^{3+} ion brownish red colour
with Mg^{++} violet colour and with Sr^{++} ion red colour is o