

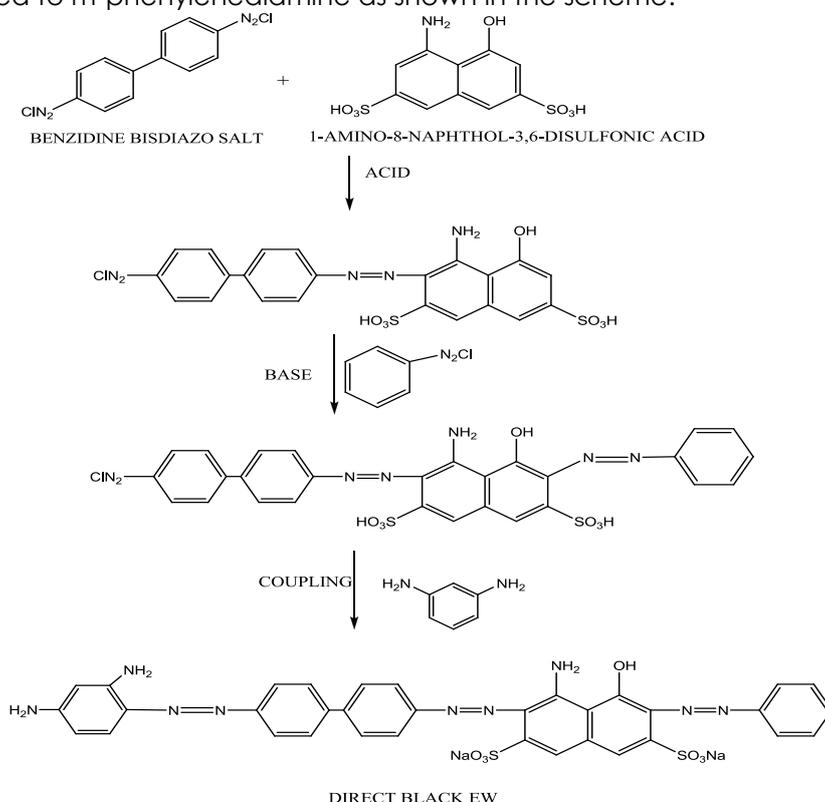
Natubhai V. Patel College of Pure & Applied Sciences
B.Sc. Semester VI
Industrial chemistry/Industrial chemistry (Vocational)
US06ICH01/US06CICV01: Dyes and intermediates

3.16 IMPORTANT SYNTHESIS OF DYES

- 1. Direct Black-EW**
[m-PDA]H⁺ ← [Benzidine] → H⁺[H-acid]OH⁻ ← [Aniline]
- 2. Naphthol Blue Black-6B**
[Aniline] → OH⁻ [H-acid] H⁺ ← [p-Nitroaniline]
- 3. Metanil Yellow**
[Metanilic acid] → H⁺ [Diphenyl amine]
- 4. Methyl Orange (Orange-III)**
[Sulfanilic acid] → H⁺ [N,N-Dimethyl aniline]
- 5. Congo Red**
(Benzidine → 2Naphthionic acid)
- 6. Indanthrene Yellow-4GK (Indanthrone)**
[(Formamide + 1,5-diaminoanthraquinone) + 2,5-dichlorobenzoyl chloride]
- 7. Eriochrome Black-T**
(4-amino-7-nitro-3-naphthol-T-sulfonic acid α-naphthol i.p.o CuSO₄ at position 1)
- 8. Eriochrome Red-B**
(4-amino-7-nitro-3-naphthol-1 -sulfonic acid → 3-methyl-1-phenyl-5-pyrazolone)
- 9. Procion Brilliant Red**
(Aniline Cyanurated H-Acid)
- 10. Tartrazine**
[Na-salt of p-hydrazino benzene sulfonic acid] + [Dioxy succinic acid] + [Na-salt of hydrazino benzene sulfonic acid]
- 11. Reactive yellow-3**
[C-acid (2-amino naphthalene 4,8-disulfonic acid) → Cyanurated m amino-acetanilide]

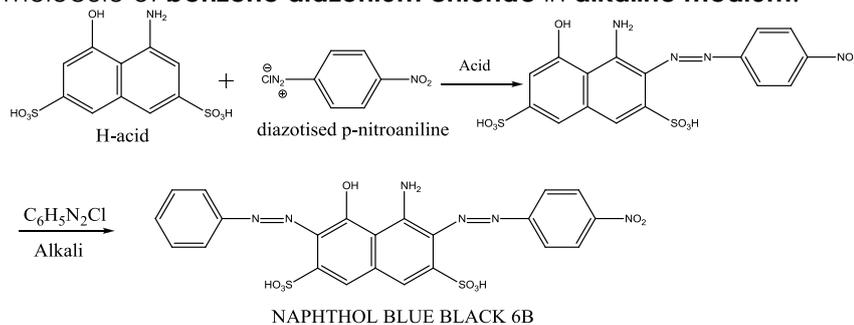
1. Direct Black EW

It is **trisazo** type dye. Prepared by **first acidic coupling** of H-acid with benzidine tetraazo, **second alkaline coupling** of the monoazo dye on H-acid part with phenyl diazonium salt and lastly the **third acidic coupling** of the bisazo diazonium compound thus obtained to m-phenylenediamine as shown in the scheme.



2. Naphthol blue black 6B/ Amino black 1 OB

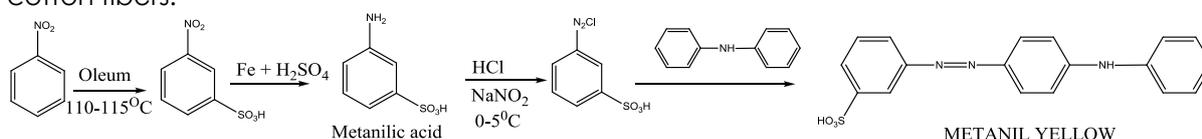
It is prepared by **coupling H-acid** (1-amino-8-naphthol-3,6-disulfonic acid) with one molecule of **diazotized p-nitroaniline** in an **acid medium** followed by **coupling** of the product with one molecule of **benzene diazonium chloride** in **alkaline medium**.



It is important acid dye used for dyeing wool for black shades of moderate fastness.

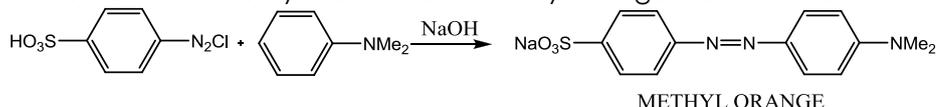
3. Metanil Yellow

It is **acidic azo dye**. The starting compound is **nitrobenzene**. It is **sulfonated** using oleum (fuming sulfuric acid) followed by **reduction** with iron and sulfuric acid gives metanilic acid. Metanilic acid is **diazotized** and **coupled** with diphenylamine gives metanil yellow. Since Diphenyl amine is insoluble in water, coupling reaction has to be carried out by emulsifying diphenylamine in water before coupling. Metanil Yellow is used for dyeing silk and cotton fibers.

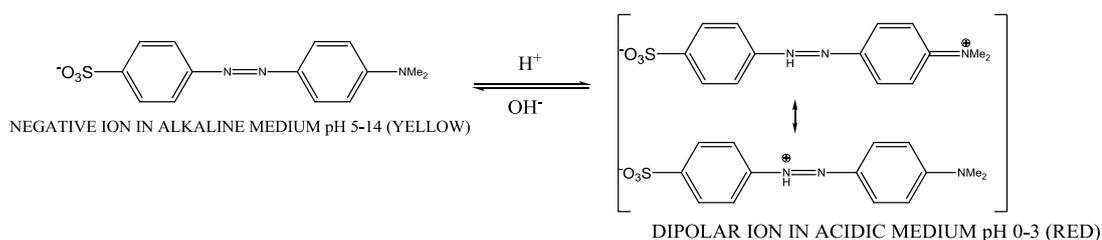


4. Methyl orange /orange III

Chemically it is sodium **p-dimethylaminoazobenzene – p' – sulfonate**. It is acidic azo dye obtained by coupling diazotized sulfanilic acid with dimethyl aniline. Dye generally isolated as sodium salt. The hydrochloride of methyl orange is called "Kelianthin"



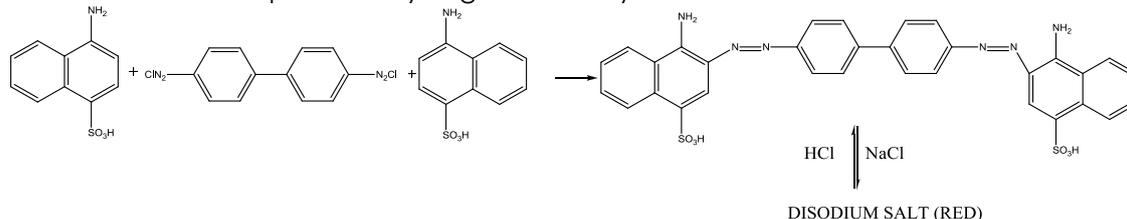
Methyl orange is not generally used as dye because it is sufficiently fast to light and soap. However, its sodium salt is used as indicator in acidimetry and alkalimetry because of its sharp colour change over a small pH range. It gives yellow colour in alkaline solution (above pH 4.4) and red in acidic solution (below pH 3.1). The change in colour of the compound in different media has been ascribed to the difference in its structure in the two media.



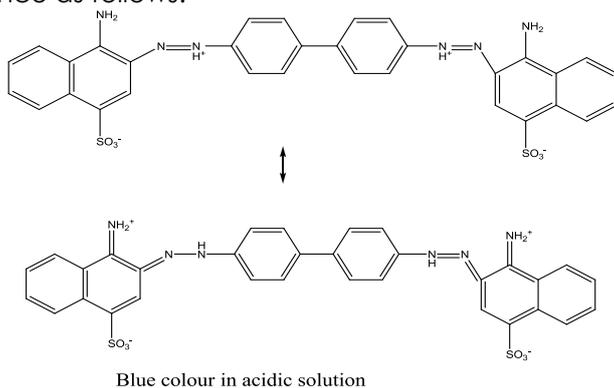
5. Congo red

It is **Basic azo dye**. It is simple benzidine bisazo dyestuff. Prepared by **coupling** tetraazotised (bis diazotised) benzidine with two molecules of naphthionic acid. Blue dye so obtained is converted into its disodium salt having red colour using NaCl.

The **red salt** is capable of dyeing cotton only.



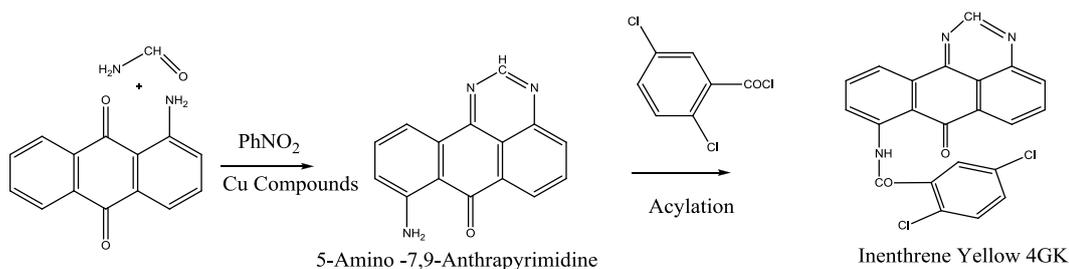
Red salt is very sensitive to acids, the colour turns from red to deep blue in the presence of strong mineral acid and dull purple in by organic acid. The change in colour from red to blue in the presence of inorganic acids may be explained due to occurrence of resonance as follows.



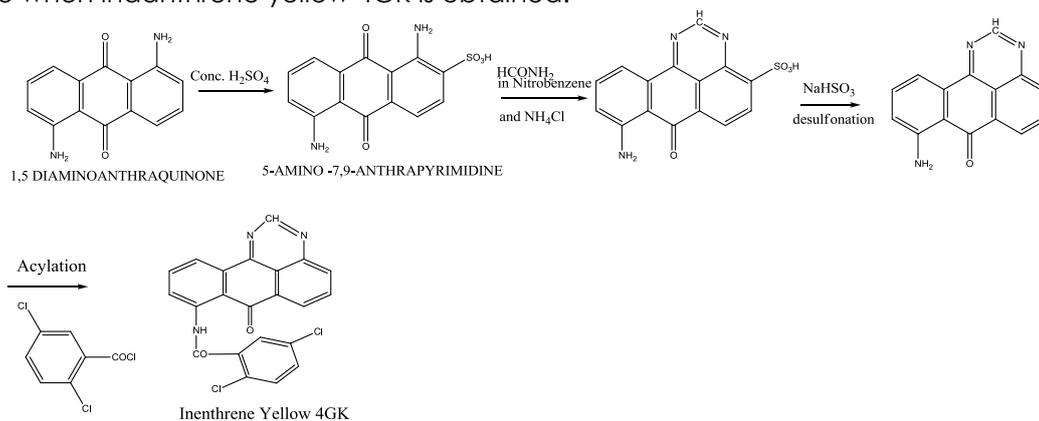
Congo red is used as an indicator in acid-base titration. Congo red paper is used for testing acidity of the solution.

6. Indenthron or Indenthrene Yellow 4GK

It is **anthraquinone vat dye**. Prepared by **condensing** 2,5-dichlorobenzoyl chloride with 1,9-anthra pyrimidine. The latter compound is obtained by condensing 1,5-diaminoanthraquinone with formamide in nitrobenzene solvent in the presence of copper compound.



It is also prepared from 1, 5 – diaminoanthraquinone which is sulfonated with conc. H_2SO_4 to give 1, 5 – diaminoanthraquinone-2-sulfonic acid. The later compound on heating with formamide in nitrobenzene in the presence of NH_4Cl followed by desulfonation with $NaHSO_3$ yields 5-amino-1, 9-anthrapyrimidine. This is acetylated with 2, 5-dichlorobenzoyl chloride when indanthrene yellow 4GK is obtained.

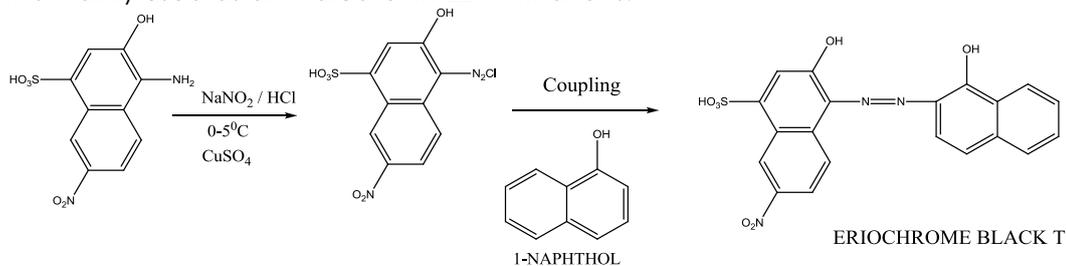


It is used as a vat dye. However it is no longer prepared.

7. Eriochrome Black T

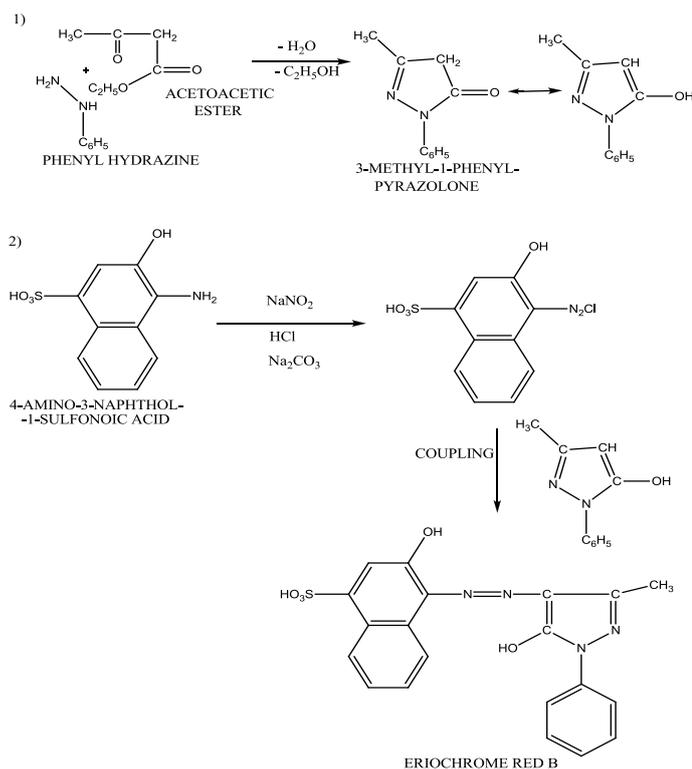
It is **mordant azo dye**. It is used in large quantities due to high light and wet fastness. Prepared by diazotizing 4-amino-7-nitro-3-naphthol-1-sulfonic acid in presence of a small quantities of $CuSO_4$ followed by coupling the product with 1- naphthol.

It is mainly used as an indicator in EDTA titrations.



8. Eriochrome Red B

It is **mordant azo dye**. Prepared by **coupling** 3-methyl-1-phenyl pyrazolone with diazotised 4-amino -3- naphthol-1-sulfonic acid. 3-methyl-1-phenyl pyrazolone obtained by condensation of acetoacetic ester with phenylhydrazine



It is fast to light and washing.

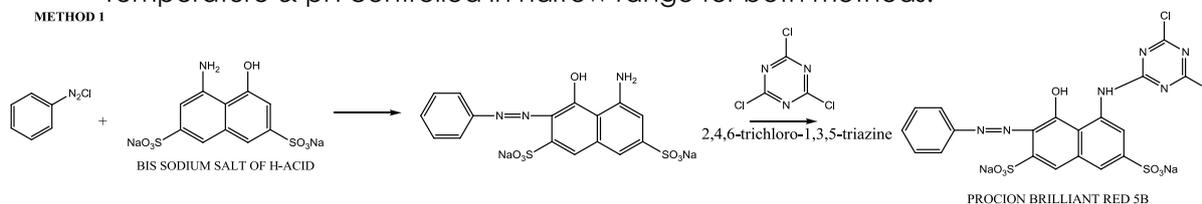
9. Procion Brilliant Red 5B

It is **reactive dye**. Prepared by **coupling** between phenyl diazonium chloride with bisodium salt of H acid. Resulting product then reacted with 2,4,6-trichloro-1,3,5-triazine gives Procion brilliant red 5B.

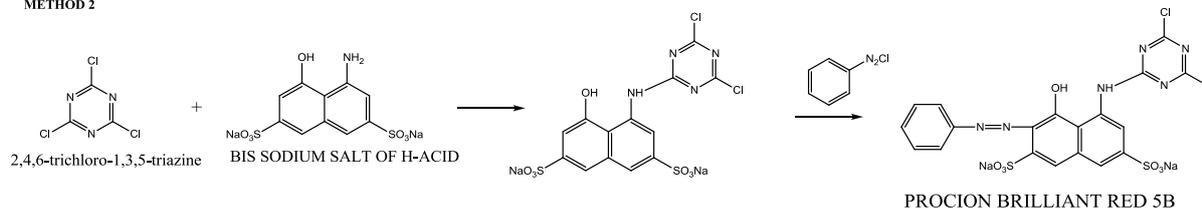
It is also prepared by reaction between 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) and Na- salt of H-acid then coupling with phenyl diazonium chloride

Temperature & pH controlled in narrow range for both methods.

METHOD 1



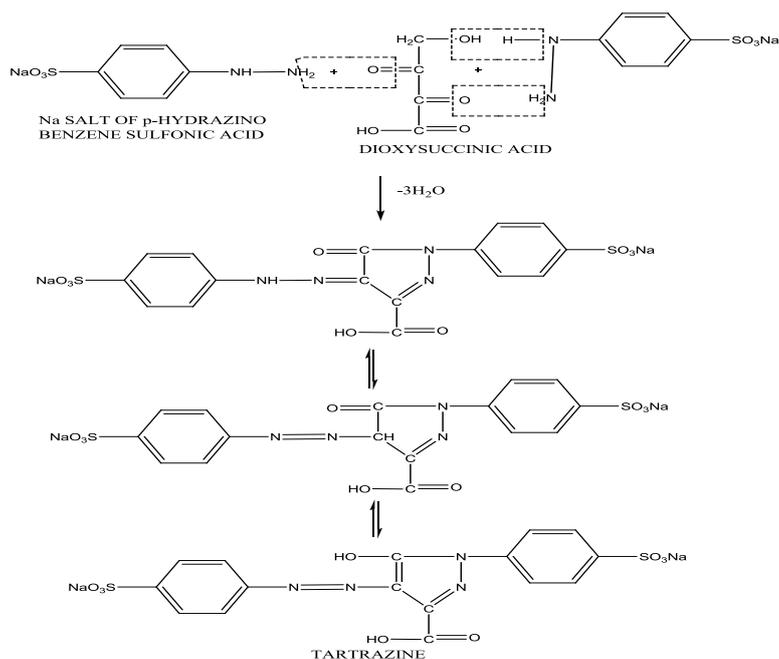
METHOD 2



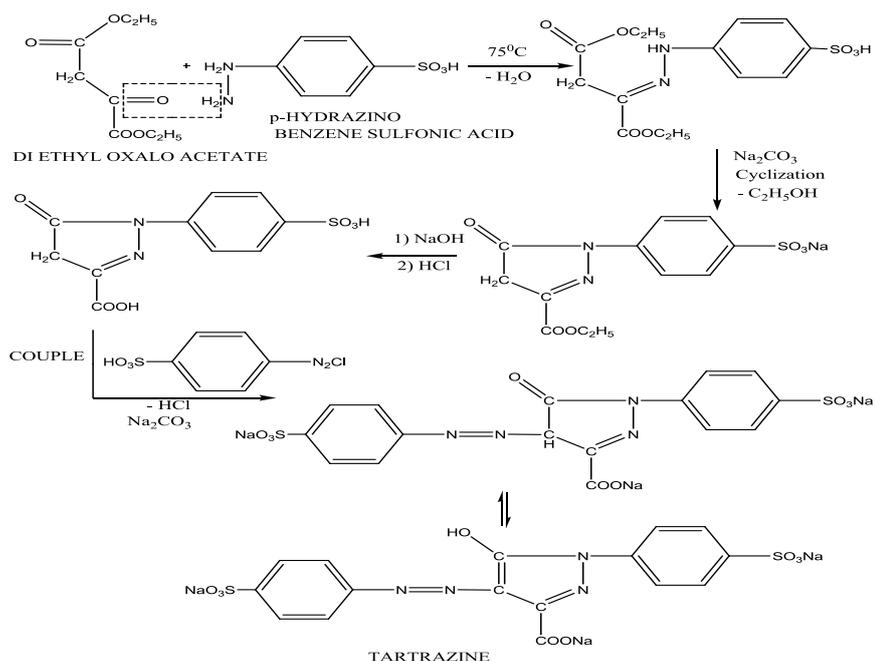
10. Tartrazine

It is an **acid azo dye**. Which may be prepared by the following **two methods**.

1. It may be **prepared by** condensing two molecules of p-hydrazino benzene sulfonic acid with one molecule of dioxysuccinic acid



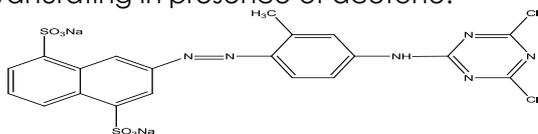
2. It may also, **prepared by** condensing one molecule of p-hydrazinobenzene sulfonic acid with one molecule of diethyl oxaloacetate. The product then coupled with diazotised sulfonic acid to yield tartrazine.



It is mainly used for dyeing wool fabric yellow with moderate fastness and silk with poor fastness.

11. Reactive Yellow 3

It is obtained by first preparing azo dye from diazotized C-acid and m-toluidine and then cyanurating in presence of acetone.



The diazotization of C-acid (1mole) is carried out by convectional method and the coupling with m- toluidine (0.99mole) is carried out in acidic medium. The pH of reaction mixture during coupling is found to have an appreciable effect on the colour and yield of

the product. Since the diazonium salt of C – acid has a very low solubility in highly acidic conditions, so either increases the volume for smooth and complete coupling or raise the pH to above 5.4 to 6.0. Raising the pH increase the solubility of the diazonium salt coupling is more smooth and yield of final dye is also increased.

The cyanuration of the dye is carried out by preparing slurry of cyanuric chloride by dissolving it in acetone to made 20% solution and the solution then added to ice water mixture. The prepared solution used for cyanuration. The use of acetone reduces the time of cyanuration.