

Natubhai V. Patel College of Pure & Applied Sciences
B.Sc. Semester VI
Industrial chemistry/Industrial chemistry (Vocational)
US06ICH01/US06CICV01: Dyes and intermediates
UNIT – 2

SYLLABUS

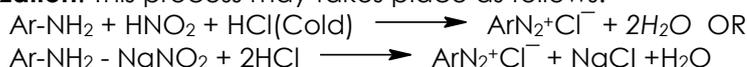
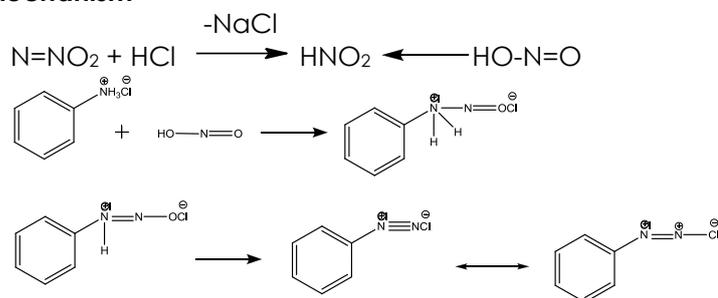
Chemistry of the following dyes with respect to general structural features and classification: Introduction, Classification and applications of Azo dyes, Acid dyes, Basic dyes and Mordant dyes.

2.0 AZO DYES**2.0.1 Introduction**

The **chromophoric system** of this class is the **azo groups -N=N-**, in **association with one or more aromatic systems**. There may be **more than one azo group** present in the dye molecule and thus one speaks of **monoazo, bisazo, trisazo, tetra-azo** and **polyazo dyes** according to whether there are one, two, three, four or more azo groups present in the dye molecule.

2.0.2 Diazotization

When a primary aromatic **amino compound** such as aniline, toluidine etc is acted on in **aqueous acid** medium by **ice-cold nitrous acid**, a **second nitrogen atom** has been **introduced** into the molecule, giving the new compound **Ar-N=N⁺Cl⁻**. This new compound Ar-N=N⁺Cl⁻ is **called diazo** compound and the **formation** of this compound is called **diazotization**. This process may take place as follows.

**2.0.3 Mechanism****2.0.4 Effects of substituent's on diazotization**

Diazotization of aromatic amine found to **depend upon** the **nature** and **position** of **substituent's** in the **nucleus** as **affecting** the **basicity** of the **amine**. For instance, relative to aniline, p-nitroaniline and 2, 4-dinitroaniline are much less basic due to the presence of electron-withdrawing **-NO₂** groups and therefore require special methods for their diazotization.

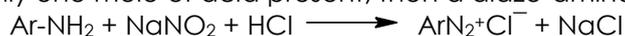
Diazotization may also give rise to **difficulties** through **low solubility** in **aqueous acid** the presence of **easily replaceable groups** such as **-SO₃H**, **-NO₂** or the presence of **easily oxidizable groups** such as **-OH**, **-CHO**. Accordingly a number of methods have been developed to overcome these difficulties.

2.0.5 Methods of diazotization

Diazotization can be carried out by different methods which are as follows.

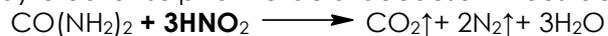
1. Direct Methods

Direct diazotization can be carried out by treating **one mole** of the **aromatic amine** with about **3 moles of hydrochloric acid**, ice is added to lower the temperature to **0-5°C** and the **theoretical quantity** of nitrite is now added as an aqueous solution. If aniline is diazotized with only one mole of acid present, then a diazo-amino compound formed.





Completion of diazotization and a slight excess of nitrous acid may be **tested** by **starch iodide paper**. The diazonium salt solution is then used for **coupling** as soon as it is produced. The excess of nitrous acid at the end of diazotization process may be destroyed either by urea or sulphamic acid because nitrous acid reacts with the second component.



As the **diazonium ion decomposes** in the **presence of metals**, the **diazotization** is **carried out** in wooden vats or rubber-lined steel vessels or glass-lined steel vessels.

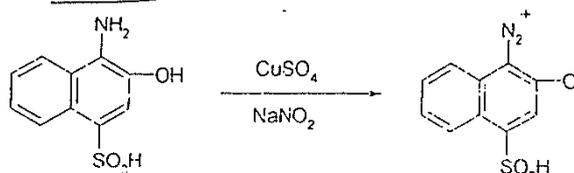
The direct diazotization may also be carried out in acetic acid with amyl or ethyl nitrite.

2. Reverse methods

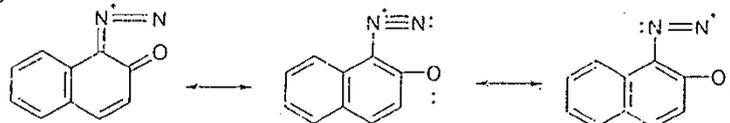
In the reverse method, a solution of **amine** and solution of **sodium nitrite** are **run into** the solution of the **acid**. This method is used for Naphthylaminesulphonic acids which give **insoluble** diazo salts due to the formation of Zwitter ion. The diazonium salts are explosive and care must be exercised in handling them.

3. Special Method

Aminophenol are readily **oxidized** by **nitrous acid** to the **quinones** and therefore, special methods are developed for diazotization. The diazotization of aminophenols is **carried out** in the **presence of copper sulphate** and **absence of mineral acids**. For example, 1-amino-2-naphthol-4-sulphonic acid is made into 25% solution, cool to 20°C. To the solution is added copper sulphate followed by sodium nitrite.



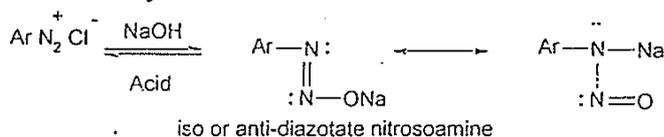
The diazo-oxide obtained is more stable than other diazo ions and may be subjected to even further reactions such as nitration, halogenation etc. The diazo-oxides undergo coupling reaction. Their resonance structures are



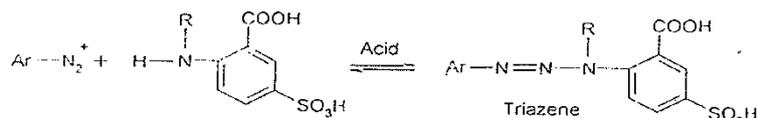
2.0.6 Stabilization of azo compounds

Most of the **diazonium salts** are **not very stable** except the nitro substituted benzene diazonium salts, diazo oxides and zwitter ions. Almost all the dry diazonim salts are **explosive**. However, there is a great need for the dyer and printer for the diazonium salts to produce different shades on the fiber by coupling. A number of methods have been developed to make stable diazonium compounds.

- Iso-Diazotates or Nitrosoamines** are produced when diazo solutions are poured into warm dilute caustic soda. These compounds are reasonably stable and are converted back to the diazo salt by treatment with acids.



- Diazoamino compounds** are produced by reacting diazonium salt with a primary or secondary amine. From these compounds, diazonium salt may be regenerated by treatment with acid. The amines employed are both aliphatic as well as aromatic. Aliphatic amines used are $\text{CH}_2\text{NHCH}_2\text{COOH}$ and other amino acids. The aromatic amines used are Sulphoanthranilic acid or 2-alkylamino-5-sulphobenzoic acids.



- Diazosulphonates** are obtained when diazonium solution is treated with naphthalene-1, 5-disulphonic acid, e.g.

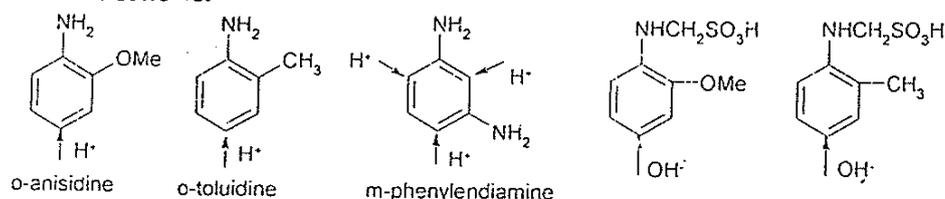
$$\text{ArN}_2^+\text{Cl}^- + \text{HO}_3\text{S-Ar}' \longrightarrow \text{Ar-N=N-O-O}_2\text{S-Ar}' + \text{HCl}$$
- The diazoarylsulphonate on redissolving in water** is in equilibrium with the diazo salt on coupling the diazoaryl sulphonate further breaks up. Diazoaryl sulphonate are prepared from diazoamino compounds, e.g. p-amino diphenylamine diazonium salt, variamine blue B and blue BB.
- Doublesalts** are obtained by treatment of diazonium solution with zinc chloride solution when the double salt $(\text{ArN}_2^+\text{Cl}^-)_2\text{ZnCl}_2$ is formed and crystallized out, e.g. benzidine, aminoazo, benzene etc.
- Stabilised fluoborates** are also obtained by treatment of diazonium solution with fluoboric acid.

2.0.7 Coupling components

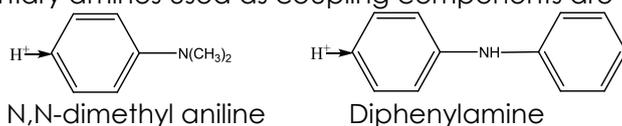
(A) Benzene derivatives

1. Amines

Primary aromatic amines are useful as coupling components. Some important examples are as follows:



The **arrows indicate the usual coupling position**. Coupling is generally **carried out under acid conditions** with an **energetic diazo component**, if **less energetic diazo components** are to be coupled with the amine, the amino groups has to be protected by first forming the methansulphonic acid by reacting the amine with formaldehyde and bisulphite. The resulting compounds may be coupled under alkaline conditions. However, the methansulphonic acid group is subsequently removed by hydrolysis. Examples of secondary and tertiary amines used as coupling components are as follows:

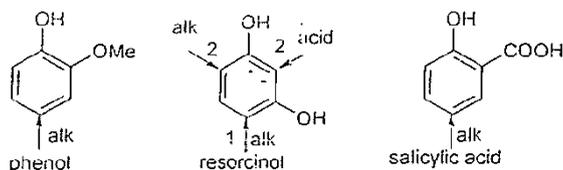


N,N-dimethyl aniline

Diphenylamine

2. Hydroxyl derivatives

Phenol couples under alkaline conditions principally in the 4 -position. In resorcinol coupling takes place in the 4 - position and then according to the pH at which the coupling is done. **E.g.** pH = 5 - 8, position 2; pH > 8, position 6. Recorcinol couples principally in the 4 - position.



phenol

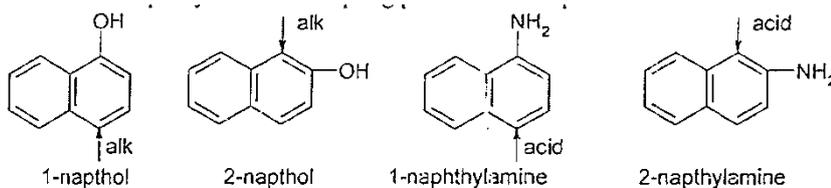
resorcinol

salicylic acid

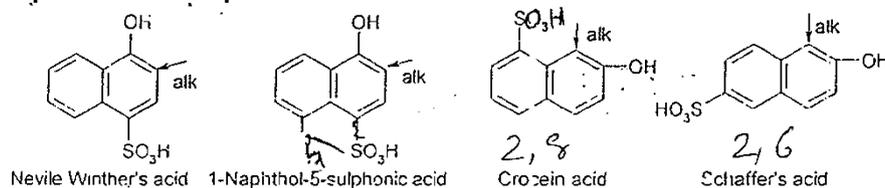
(B) Naphthalene derivatives

1. Naphthols and Naphthylamine

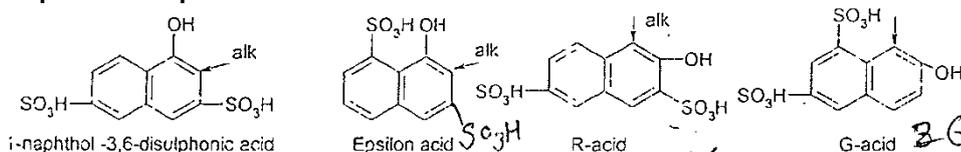
Coupling positions of naphthols are shown as



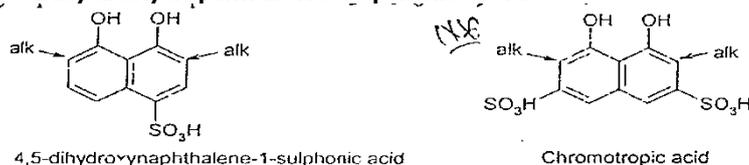
2. Naphtholmonosulphonic acids



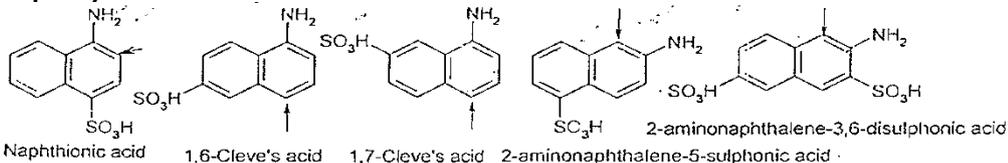
3. Naphtholdisulphonic acids



4. Dihydroxynaphthalene sulphonic acids

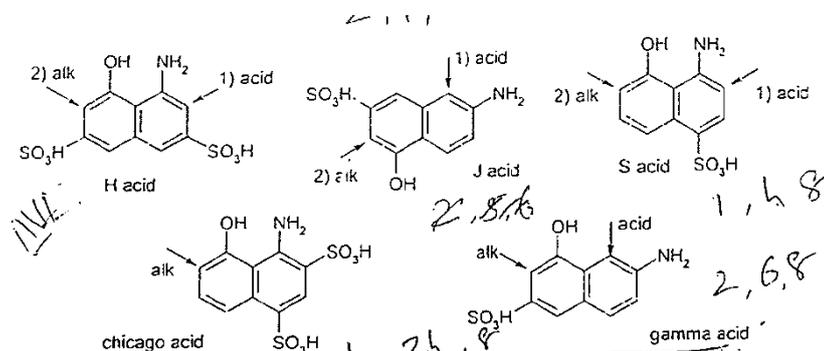


5. Naphthylamine sulfonic acid



6. Amino naphthol sulphonic acids

An example of these is H-acid from which hundreds of azo dyes are prepared which are widely used for dyeing wool, cotton, leather dyes.

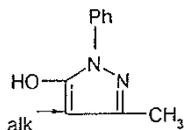


7. Methylphenyl pyrazole

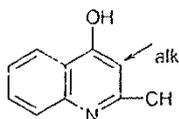
It couples at position 4. It is used in the manufacture of direct and acid dyes and especially in mordant dyes.

8. Acetoacetanilide

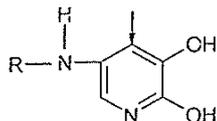
It is used for making a number of direct and acid dyes.



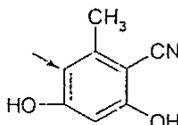
9. Quinoline – 2,4 – diol



10. Dihydroxyquinolines



where R = alkyl



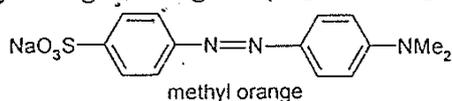
2.0.8 Types of azo dyes

The **azo dyes prepared** and **used** are **very large in number**, also their **structures** are **largely varied** and **so** they are **further classified according to the fibers** as follows.

1. Acid azo dyes
2. Basic azo dyes
3. Direct or substantive azo dyes
4. Ingrain azo dyes
5. Mordant azo dyes
6. Synthetic fiber dyes
7. Stilbene – azo dyes

1. Acidic azo dyes

These dyes have been characterized by the **presence** of an **acidic group** such as $-\text{SO}_3\text{H}$, $-\text{COOH}$ or phenolic $-\text{OH}$ group. The **acidic group** makes the dye **more soluble** and **act** as **auxochromes**. **E.g.** Methyl orange /Orange III (Sulfanilic acid to N,N-dimethyl aniline.)



2. Basic azo dyes

These have $-\text{NH}_2$ or $-\text{NH-R}$ groups are the **auxochrome**. The chromophoric system is present as cations. **E.g.** Aniline Yellow (Aniline to Aniline)

3. Direct or substantive azo dyes
The azo dyes described earlier are used to dye the proteinous fibers (e.g. Wool, Silk and leather) directly but they need mordant for dyeing cellulosic fibers (e.g. Cotton, linen, paper etc). However, certain azo dyes are known which could dye directly the cellulosic fibers without a mordant such azo dyes are called direct or substantive azo dyes. **E.g.** Congo-Red (Benzidine to 2-Naphthionic acid).

4. Ingrain azo dyes

These are **water insoluble azo dyes** which are formed on the fiber. They are prepared by dipping the fabric in an alkaline solution of 2-Naphthol containing Turkey red oil, drying it and then immersing in a solution of the diazotized amine. The most important example of this group is Para red (p-NA to β -naphthol).

5. Mordant azo dyes

These are the azo dyes, which when **fixed** on the **fiber**, are capable of forming **complex metallic compounds** when **treated** with **metallic salts** such as sodium dichromate, sodium chromate or chromium fluoride. Chromium is the most widely used metal in mordant azo dyes. Most of the dyes belonging to this group are monoazo dyes but they include a few

diazo dyes. Their great importance is due to 'their high fastness' to light and washing. **E.g.** Diamond black-F (5-amino salicylic acid \rightarrow 1-naphthylamine \rightarrow 1-naphtho-4-sulfonic acid).

6. Synthetic fiber dyes

Several dyes are known which are used to dye synthetic fibers such as Rayon, Terylene, Nylon, Polyacrylonitrile etc. These may be acidic, basic or, disperse dyes **E.g.** Cellitone scarlet-B. (p-NA N-ethyl-N(β -hydroxy ethyl)-aniline).

7. Stilbene azo dyes

These are **yellow and orange direct azo dyes** used for Cellulosic fibers. Although these dyes have azo groups, they are not prepared by process diazotization and coupling.

2.0.9 Subclasses of Azo dyes

Azo dyes can also put into various subclasses such as monoazo, bisazo, trisazo, mordant azo, stilbene azo, polyazo and pyrazolone.

2.0.10 Nomenclature used in the subclasses of azo dyes (LAPWORTH'S NOTATION)

In the following discussion of various subclasses of azo dyes, Lapworth's system is used to represent general structure of azo dyes. In this system, we use the following notations.

A: It represents an Arylamine used as diazonium components, further such components used are denoted by A1, A2 etc. Examples of A are aniline, O-toluidine etc.

D: It is an Aryldiamine like benzidine having two diazotizable groups. Examples of "D" are benzidine, 4,4'-diaminostilbene-2,2'-disulphonic acid etc.

E: It is the second component or coupling component. Example of "E" are phenol, β -Naphthol, dimethylaniline etc.

Z: It is a coupling component having dual coupling positions. Examples of Z are H-acid, gamma acid, J acid etc.

T: It is a coupling component having three coupling position. Examples of "T" are Resorcinol, m-phenylene diamine.

M: It is the middle component having one coupling position and one diazotizable amine which can further couple with a coupling, component. Examples of "M" are 1-naphthylamine, J-acid etc.

2.0.11 Different types of azo dyes

A \rightarrow E

E.g. Orange-II (Sulfanilic acid \rightarrow β -naphthol)

A \rightarrow Z \leftarrow A1

E.g. Naphtho Blue Black-6B (Aniline \rightarrow H-acid \leftarrow p-NA)

E1 \rightarrow D \leftarrow E

E.g. Congo Red (Naphthionic acid \leftarrow Benzidine \rightarrow Naphthaionic acid)

A \rightarrow M \rightarrow E

E.g. Cloth Red-B (ortho toluidine \rightarrow ortho toluidine \rightarrow 1-Naphthol-4-sulfonic acid means NW-acid).

A \rightarrow Z-L-Z \leftarrow A1

E.g. Chlorazol Scarlet 4-BS (Aniline \rightarrow J-acid Urea \leftarrow p-amino acetanilide)

2.1 ACID DYE

2.2 BASIC DYE

2.3 MORDANT DYE