

Dyeing with Azoic dyes

Azoic dyes

- The dyes containing insoluble azo group ($-N=N-$) are known as azoic dyes.

These dyes are not found in readymade form. Azoic dyes are produced by a reaction between two components. The components are:

1. Coupling Compound (Naphthol)
2. Di-azo –compound or diazo base or diazo salt.

How they are formed

The colored substance formed from this colorless compound is insoluble in water and washing fastness of this shade is excellent.

They have excellent coloring properties, again mainly in the yellow to red range, as well as lightfastness. The lightfastness depends not only on the properties of the organic azo compound, but also on the way they have been absorbed on the pigment carrier.

- Since the application is carried out in an aqueous medium, the two compounds combine in the solution phase, the pigment is partly loosely deposited on the fibre surface and partly it is suspended in the dye bath, the surface deposition leads to poor rubbing fastness

Reaction of Azoic Dye

- **Naphtholation:**

Naphthols are insoluble in water and they are converted into water soluble compound by treating with alkali.

Diazotization:

A base containing amino group ($-NH_2$) reacts with the $NaNO_2$ (Sodium Nitrite) to form a solution of diazonium chloride of that base in presence of excess HCl at $0-50^\circ C$ temperature.

Coupling/ Developing:

The impregnated material is treated in a bath containing diazonium solution to carry out to coupling and thus color is produced inside the fabric. The pH maintaining is important.

Azoic coupling

Most of the azoic coupling components are arylides of Beta –oxynaphthoic acid(BON) also referred as Brenthols

Any azoic coupling componenet can be combined with any diazotised base so that 30 different Naphthol and 50 bases, can yield 1500 possible combinations

Naphthols

- Naphthols differ widely from one another in their affinity or substantivity for cotton fibre
- They can be classified as:

1.Low substantivity Naphthol

2. Medium substantivity Naphthol

3.Higher substantivity Naphthol

4. Still higher substantivity Naphtho

Substantivity of Naphthol can further be increased by adding electrolyte like Common salt or Glauber's salt

Substantivity of Naphthols

- With high substantivity of Naphthol, only small residue of this product will remain unutilized in the bath after application
- With low, medium and moderate substantivity naphthols usually salt is added to increase their substantivity

Method of dissolution of naphthols

There are two method : Hot and Cold

In the hot method, the naphthol is pasted with turkey oil, the required amount of NaOH solution is added and boiling water is poured.

In the cold dissolving, the naphthol is stirred with required amount of methylated spirit, sodium hydroxide used is less than that in Hot process, cold water is added to get clear solution

Naphtholates

- Hot dissolving method gives good results, but is more laborious than the cold dissolving method.
- More concentrated solutions of Naphthols can be prepared by cold dissolving method, however this is more expensive
- Concentrated solutions of naphtholates are not very stable, so can not be stored for long time, must be added soon to the naphtholating bath

Use of caustic soda

- Azoic coupling components are insoluble in water and have to be converted into their alkali salts to dissolve them
- Usually caustic soda solution is used for the purpose
- The two acidic hydrogen can be replaced by sodium

High degree of brightness

- Because of high degree of brightness, ease of application and excellent fastness properties (except rubbing fastness which can be improved by using certain auxiliaries) azoic combinations (naphthol and bases) are widely used in printing on cellulose fiber fabrics.
- Azoic dyes are used for producing bright shade of color such as orange, red, scarlet, navy blue, and black color.

Typical procedure

- **For naphtholation:**

- 1) For making naphthol solution, at first naphthol and glycerine are added in dye bath.
- 2) Then NaOH is added into the bath.
- 3) Finally salt and water are added into the bath.
- 4) Then fabric is immersed into this solution for few minutes. And the fabric becomes naphthaled.

For base recipe:

- 1) At first required amount of base, HCl, NaNO_2 are mixed another dye bath at 0-50C (with ice).
- 2) Then acetic acid and sodium acetate are added into the dye bath. And mixed them very well.
- 3) Finally thickener and required amount of water is added and stirred them very well for getting required viscosity.

Azoic dyes in printing

- **Printing process:**

The naphtholated fabric is prepared then it is printed with base printing paste by block and screen printing method.

After treatment :

After printing the printed fabric is dried at 100-105 for 5-10 minute in a dryer.

- If the naphtholation process is not so sufficient. Then the printing becomes uneven.

A Typical recipe for making Azo dye

- Sulfanilic acid, 1-naphthylamine, 2-naphthol sodium nitrite, 2 N NaOH, 2 N H_2SO_4
The following solutions are prepared:

Sulfanilic acid solution: 1.7 g of sulfanilic acid in 50 mL in of 2 N H_2SO_4

Sodium nitrite solution: 0.6 g of NaNO_2 in 10 mL of dist. H_2O

1-Naphthylamine solution: 0.7 g of 1-naphthylamine in 50 mL of 2 N H_2SO_4

2-Naphthol solution: 0.7 g of 2-naphthol in 50 mL of 2 N NaOH

How it can be made in Laboratory

- A crystallizing dish is half filled with ice. Four beakers containing the following solutions are placed in a ice bath:
beaker 1: 50 mL of an acidic solution of sulfanilic acid
beaker 2: 10 mL of an aqueous solution of sodium nitrite
beaker 3: 50 mL of an acidic solution of 1-naphthylamine
beaker 4: 50 mL of an alkaline solution of 1-naphthol

The sulfanilic acid solution is mixed with the aqueous solution of sodium nitrite while stirring. Equal volumes of the mixture are poured into the beakers 3 and 4.

Dyeing cotton with Azo dyes

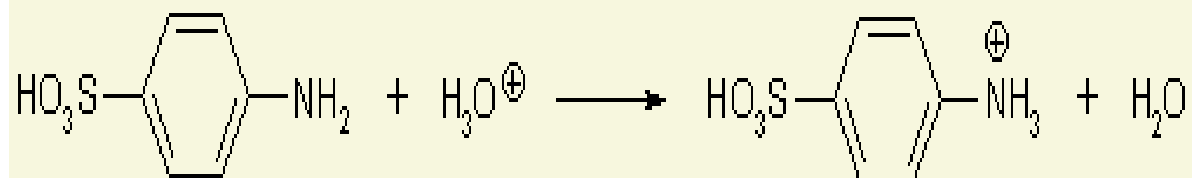
- For example, cotton fabric, impregnated ("padded") with the sodium salt of 2-naphthol, is immersed in a buffered solution of the diazonium salt; the color develops immediately.
- Unfortunately, sodium 2-naphtholate has only a low affinity for cotton, hence the poor fastness towards washing, rubbing, etc.
- Coupling components of greater affinity for cotton have been developed from 2-hydroxy-3-naphthoic acid

Naphthol AS

- The resulting dyes produced from 2-hydroxy-3-naphthoic acid (Naphthol AS) have much improved fastness properties in comparison with those from 2-naphthol; a greater range of colors is also obtainable.
- Because of the high affinity of Naphthol AS and its analogs there is little or no running of the resulting dyes into each other when cotton padded with more than one coupling component is immersed in the diazonium salt solution.
Several shades may thereby be simultaneously developed

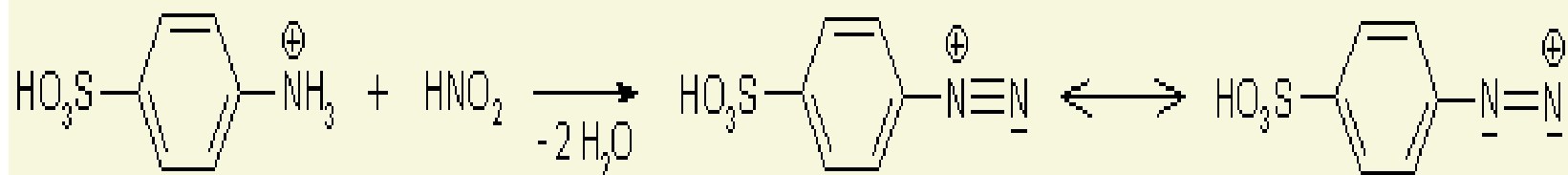
Development of the dye

- The preparation of the specimen for dyeing may be performed as follows:
 - (a) pieces of cotton fabric (padded with different coupling components, and dried) may be sewn together, or in close proximity on a piece of supporting material; or
 - (b) The solutions of the coupling components - -
may be applied as spots or as lettering etc. on the cotton which is then dried in the air or with gentle warming



sulfanilic acid

(1)

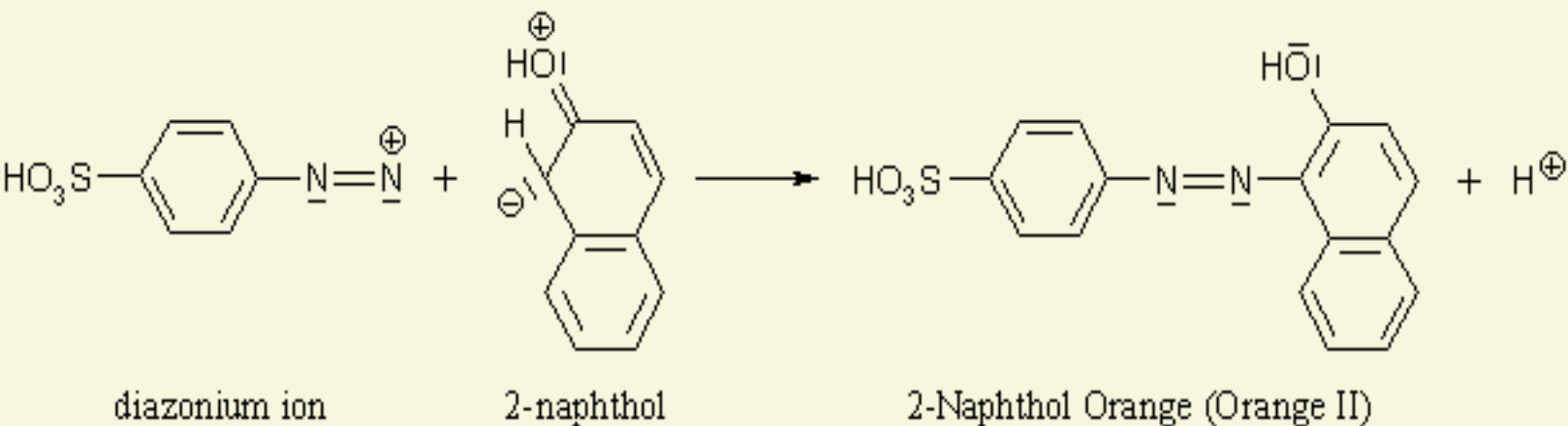


nitrous acid

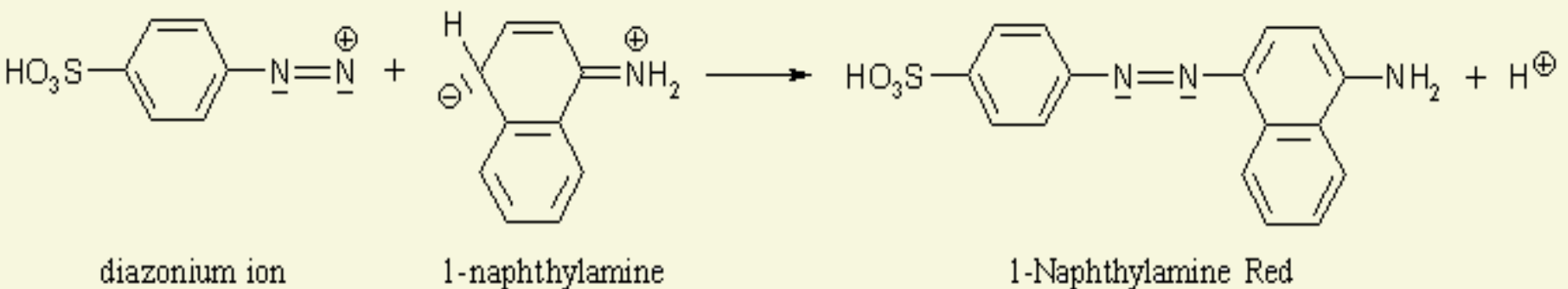
diazonium ion

Diazotation: When primary aryl amines are reacted with nitrous acid (generated from NaNO_2 in combination with H_2SO_4) a reaction occurs which makes a diazoniumion (1). The reaction takes place under freezing conditions.

Coupling reaction: The diazotized sulfanilic acid reacts with 2-naphthol and 1-naphthylamine to produce an acidic and basic azo dye alternatively (2). The azo coupling represents an electrophilic aromatic substitution. The diazonium cation is a relatively weak electrophile. So the aromatic ring which it attacks must have a activating group such as - OH and - NH₂. Electron withdrawing groups on the aromatic ring of the diazonium ion facilitate the substitution reaction. Electrophilic substitution of 2-naphthol occurs preferentially at the 1-position. The NH₂ group in 1-naphthylamine activates the 2- and 4-position.



(2)



Hazardous nature of Azo dyes

- Certain azo dyes can break down under reductive conditions to release any of a group of defined aromatic amines. Consumer goods which contain listed aromatic amines originating from azo dyes were prohibited from manufacture and sale in EU countries after the German ban in 1997. Many azo pigments are non-toxic, although some, such as dinitroaniline orange, ortho nitroaniline orange, or pigment orange 1, 2, and 5 have been found to be mutagenic. Likewise, several case studies have linked azo pigments with basal cell carcinoma.