## Indigo Dyes

Indigo: It is the parent compound of indigo based dyes and has been used from long time back. An interesting fact about these dyes is that the Egyptian mummy clothes, which are five to six thousand years old, were dyed with it. Indigo was originally extracted from the plants of indigoera group. The leaves from these plants were covered with water and allowed to stand for several hours. Enzymes present in the plants brought about fermentation. The fermentation eventually converts the β-glucoside of indoxyl (known as indican) of the leaves into indoxyl and glucose. Upon exposure to air the indoxyl group was oxidized to indigo. Natural indigo contains an isomer of indigo known as indirubin and other impurities. Indigo is a dark blue crystalline solid, which is insoluble in water and

most of the organic solvents. However it is damn useful for dyeing cotton by vat process.

## Preparation of Indigo

It cam be obtained with the help of different synthetic routes like:

1. From aniline and chloroacetic acid: Aniline is allowed to react with chloroacetic acid to give N-phenyl glycine. This glycine derivative is now treated with NaOH and sodamide at 523 K to form indoxyl which upon aerial oxidation gives the dye molecule.

Now a days N-phenyl glycine is obtained by the chemical combination of aniline and the bisulphite derivative of formaldehyde at 323-333 K. It is followed by treatment with aq NaCN and subsequent acid hydrolysis. This method is advantageous because the percentage yield is better.

This modern method is schematically shown below,

Baselphite addition product

2. From anthranilic acid and chloroacetic acid: It is the anthranilic acid which upon treatment with chloro acetic acid gives an intermediate. Subsequently, it is fused with NaOH and sodamide to produce indoxylic acid, which is an unstable compound. Further decarboxylation of indoxylic acid gives indoxyl which upon aerial oxidation gives the required dye.

$$\begin{array}{c} H \\ \downarrow \\ C=O \\ \downarrow \\ NH_2 \\ Anthranilic \\ acid \\ \end{array}$$

$$\begin{array}{c} CH_2-COOH \\ \downarrow \\ NAOH, \\ \downarrow \\ NaOH, \\ \downarrow \\ NaOH, \\ \downarrow \\ NaNH_2, \\ \Delta \\ \end{array}$$

$$\begin{array}{c} C-OH \\ \downarrow \\ \downarrow \\ C-COOH \\ \downarrow \\ \downarrow \\ Indoxyl \\ dimerisation \\ O_2 \\ \end{array}$$

$$\begin{array}{c} C-OH \\ \downarrow \\ Indoxyl \\ (unstable compound) \\ \end{array}$$