Chemical Structure:

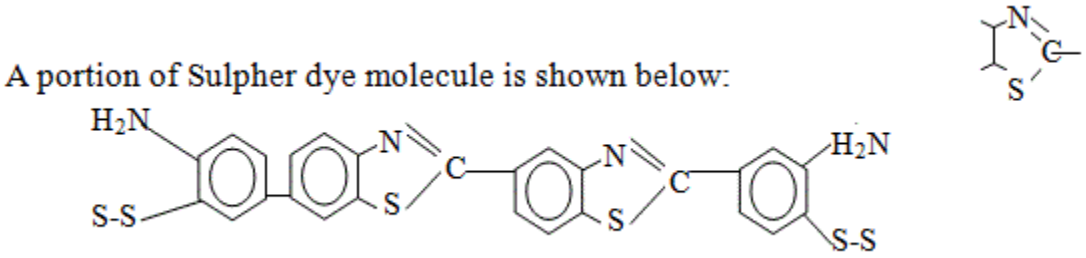

Fig: Chemical structure of sulfur dyes

The exact **chemical structure of sulfer dyes** is not known, but these dyes contain sulfur as an integral of the chromophore as well as in the polysulphide side chains. These are produced by thionisation or sulphurisation of organic intermediates containing nitro and amino groups.

Properties of Sulphur Dyes:

These are water insoluble dyes and have no affinity for the cellulosics as such, but solubilised when treated with a weak alkaline solution of sodium sulphide or any other reducing agent to form a leuco compound. These leuco compounds are water soluble and have affinity for the cellulosic materials such as cotton, viscose, jute and flex etc. These dyes are absorbed by the cellulosic material in the leuco form from aqueous solution and when oxidized by suitable oxidizing agents, got converted into insoluble parent dye, which is fast to normal color fastness parameters.

Main Properties of the Sulfur Dyes are as Follows:

1. Economical dyeing with excellent tinctorial value and good build up properties.
2. Good overall **colorfastness** properties such as **wash fastness**, light fastness, perspiration fastness etc. Moderate fastness to crocking and poor fastness to chlorines **bleaching agents** such as bleaching powder and sodium hypochlorite.
3. Limited shade range to produce only dull shades and there is no true red dye in the range.
4. These dyes can be applied by exhaust, semi continuous or continuous dyeing methods on garment, yarn, knits, fabric as well as loose stock etc.
5. Available in powder, granules and liquid forms.
6. Sulphur black 1 is the major black dye used world wide for dyeing of cellulosics.
7. The conventional dyeing process is not environment friendly due to pollution problems of sodium sulphide as well as sod/pot. Dichromates.
8. When dyed by using non polluting reducing and oxidizing agents the process is environment friendly.

Types of Sulphur Dyes:

There are three classes of **sulfur dyes**, which are available commercially,

1. Conventional water insoluble dyes which have no substantivity to cellulosics.
2. Solubilised sulfur dyes, which are water soluble and non substantive to cellulosics.

3. Pre-reduced sulfur dyes, in the stabilized leuco compound form, which are substantive to cellulosics.

Application of Sulphur Dye:

Mechanism of the Sulphur Dyeing

The application of the sulfur dyes involves several steps, which are described as given below,

1. Dissolving the dyestuff:

The dye is taken in an SS vessel (size of the vessel should be selected as per the quantity and solubility of the dyes) and pasted well with a good alkali stable wetting agent and small quantity of soft water. A required quantity of soda ash may be added to neutralize any acid formed in the dyestuff during storage.(if the acid is not neutralized , it will react with the sodium sulphide , resulting into formation of H2S gas, which will result into incomplete and poor reduction of the dyes). It is very important that the dye dissolution must be complete otherwise particles of the undissolved dyes may deposit on the surface of the substrate resulting into patchy dyeing and poor rubbing / washing fastness.

2. Reducing the dyes to form a leuco compound:

Chiefly sodium sulphide is used as a reducing agent for the sulfur dyeing . The quantity of the reducing agent depends upon the shade depth and M:L of the bath. For complete reduction the required quantity of the sodium sulphide is dissolved in a separate container and solution is allowed to settle for 10-15 min. before decanting the clear solution into the dye dissolving vessel. Further boiling water is to be added to make up the required volume , then heated to boil for 10-15 minutes either by live steam or indirect heating , for complete reduction of the dyestuff.

3. Dyeing with the reduced dyes:

It is advantageous that the goods are scoured well before dyeing ,to have a satisfactory absorbency for better penetration. The dye bath is kept ready with small quantity of the alkali stable and aompatible wetting agent , a dye bath stabilizer , sodium sulphide and caustic soda or soda ash to maintain the alkalinity of the dye bath. The dye solution is then added through a filter cloth slowly over 15-25 minutes and then run for another 15 minutes at 40-50 oC , then temperature is raised to 60 oC and electrolyte is added in at least 3 portions. The quantity of salt added is depends upon the type of shade , depth and dyestuffs , however a maximum quantity does not exceed more than 15 gpl .The temperature is then raised to above 80 oC or even boil depending upon the dyes and kept for sufficient time to get the desired shade.

After getting the correct shade the bath is either dropped by draining the contents or by collecting it in the storage tanks for reuse after replenishing with fresh dyestuffs.

After washing the material is given a hot wash at 70 0C .

4. Oxidation back to the parent dye:

The oxidation is done to reconvert the leuco compound back to insoluble parent dye. There are number of methods available for oxidizing the leuco compound which are used either

independent or in combination, such as

a. Oxidation by exposing the dyed material to atmospheric oxygen.
b. Oxidation by the dissolved oxygen in the fresh water.
c. Chemical oxidation , by employing different oxidizing chemicals, such as

I. acetic acid
II. sodium perborate in cold at neutral pH.
III. Hydrogen peroxide and acetic acid.
IV. Potassium or sodium bicarbonates and acetic acid.

5. Washing off the unexhausted dyestuff:

With an objective of achieving the highest possible color fastness results such as washing , rubbing , light and perspiration , the material is washed and rinsed several time with fresh water to remove maximum possible loose residual dye as well as sodium sulphide from the material. At the end of the washing process the water should be clear , with no further leaching out color .

6. After treatment:

After oxidation and hot wash , the material is neutralized with soda ash to adjust the pH and then soaping treatment is done with a neutral soap and soda ash at boil. Followed by a hot wash at 85 0C

7. Dye fixing treatment:

Optifix F(clariant) is a cationic dyefixing agent , which is applied in alkaline conditions (at a pH of 10-11) , and is a suitable dyefixer for sulphur dyed material to improve the color fastness.

8. Softening:

A suitable (compatible) softener can be applied to the dyed material as per the intended end use and dyestuff applied.

9. Final treatment:

To avoid the tendering of the dyed material final wash is given to maintain a slight alkaline pH by a weak base or acid neutralizing agent at the end without further washing. Following treatments are recommended,

- Soda ash wash 2-3 gpl
- Sodium Acetate 2-3 gpl
- Tetrasodium pyrophosphate 5.0 gpl
- Lime and tannic acid treatment

10. Use of Standing Bath:

Since a large quantity of the dye always present in the unexhausted form in the spent liquor , this remaining dye can be reused , after replenishing with fresh dye. This system is particularly suitable when producing repeated lots of the same shade with a single dye , such as black.

The dye liquor at the end of dyeing cycle is collected in the tanks, to replenish the bath a separately made dye solution is added and calculated quantities of sodium sulphide , soda ash as

well as salt are added. The final volume is made up to the required level and reused. Usually a 50 –70% dye is replenished in case of blacks.

The spent bath use is not recommended in case of mixture shades , due to difference in the exhaustion and fixation of individual dyes.

Common Problems and Corrective Action

1. Poor wash and rubbing fastness

Poor washing and rubbing fastness is generally caused by improper color dissolution ,color precipitation, poor solubility of the dyes, poor and insufficient washing after dyeing of unexhausted dyes and poor or insufficient soaping treatment. To get overall good fastness properties:

- The dye dissolution must be complete and it should be filtered before adding to the dye bath, because insoluble dye particles ,if present , will stick at the outer surface of the substrate causing unleveled dyeing and poor wash and rub fastness.
- The color should be dissolved in sufficient quantity of water , by keeping in mind the maximum solubility of the dye.
- The water and the salt should be free from calcium and magnesium , which, if present will make insoluble inert salts , which precipitates especially in the closed dyeing machines, in the form of sludge.
- The washing after dyeing and soaping treatment must be efficient to clear all the unused dye as well as chemicals , before going to the next operation such as oxidation and neutralization respectively.

2. Bronziness

There are various reasons for bronziness in the sulphur dyed material such as, in sufficient quantity of sodium sulphide or reducing agent , resulting into quick oxidation of surface dyeing. The presence of excess dyestuff on the material caused by high concentration of of dye or electrolyte , delay between dropping of bath and washing , oxidation step. Following are the corrective actions for correcting and avoiding the **bronziness problem,**

- Proper dissolution of the dyestuff.
- Thorough washing and treatment with reducing agent before oxidation.
- Use of surfactants, sequestering agents, dispersing agents , dye bath stabilizers, and anti oxidants in reducing bath.
- Using sufficient and calculated quantity of reducing agents.
- Using appropriate quantity of electrolyte e.g. less than 15 gpl.
- After treatment witj 2-3 gpl TR oil+ 1-2 cc/ltr of ammonia in luke warm bath , to overcome the problem.
- Treatment with soap solution at boiling temperature .
- Using a blank bath of sodium sulphide .

3. Tendering

Tendering means the loss of strength or degradation of cellulosic materials upon storage. The tendering is caused by the acid formation from the free sulphur present in the dyed material by the action of moisture and air. The acid produced reacts with cellulose and degrade it , resulting in loss of strength. The tendering can be minimized by giving after treatments with acid neutralizing agents or by weak alkaline washing at the end of dyeing process.

4. Poor color value

Poor color value is caused by insufficient amount of reducing agent , presence of calcium salts in water and salt, over reduction of dyestuff , over oxidation etc.

5. Correction of faulty dyeing

If the dyeing results are unlevel , then these can be corrected by

- Leveling the dyed material by running in a blank bath containing excess sodium sulphide, dispersing ,sequestering agent, wetting agent at a temperature of 80-90 degress, this treatment will partially strip the color , which can be adjusted in a fresh bath. Or alternatively the partial stripping can be done by using caustic soda 5 gpl and hydros 5 gpl at a higher temperature than the dyeing temperature.
- For poorly leveled material , the material is treated with sodium or calcium hypochlorite , in which it is treated with 2-3 gpl available chlorine at room temperature, followed by thorough wash and neutralization and antichlore treatment.

Water Quality for Sulphur Dyeing

The use of soft water with less than 50 ppm hardness is preferred which should be free from calcium salts, but in case only hard water is available , a sequestering agent based on sodium hexametaphosphate or EDTA should be used. These chemicals avoid the formation of insoluble metal-dye complexes which cause poor rubbing fastness and uneven dyeing.

Other Recommended Chemicals in Dyeing

1.Wetting agents:

Normaly 1-2 gpl wetting agent is used for good penetration, in the dyeing bath.Wetting agents used must be compatible with the dyestuff, particularly in combination shades. The wetting agents must be low foaming and alkali stable at high temperature. Unsuitable wetting agents adversely affect the dye bath , inhibiting the dye uptake or precipitating the leuco compound of the dye.

Normally 1-2 gpl of wetting agents are used in the dyeing bath for good penetration.

2. Dispersing or dye bath conditioner:

These are used to impart the leveling effect as well as to keep the dye in dispersed form ,to avoid the dye aggregation and precipitaion.

Generally naphthalenesulphonic acid –formaldehyde condensate, ligninsulphonates and sulphonated oils are used in sulphur dyeing.

Dyeing with Pre-reduced Liquid Sulphur Dyes

The pre-reduced sulphur dyes are available as stabilized liquids, which have substantivity for the cellulosic, materials .

Main properties of Pre –reduced Dyes

- No dissolution required, therefore cleaner environment and working conditions.
- No use of sodium sulphide, therefore lesser smell.
- Low salt additions are required.
- Lesser pollution loads.
- Easier washing off of the reducing agents ,therefore easy oxidation.
- Less staining and contaminations of the dyeing machines.
- Good storage stability and water solubility.

These dyes are recommended for exhaust dyeing of cotton in loose fiber, yarn, fabric and continuous dyeing, such as rope dyeing.

The use of non polluting chemicals and by Reusing the spent liquor dye bath, the dyeing becomes less polluting and environmental friendly. There are two major pollutants generated in classical sulfur dyeing procedure,

a. sodium sulfide in the reducing step
b. Potassium/ sodium dichromate in the oxidation step.

Both these chemicals are potentially hazardous for the environment, but can be replaced by environment friendly, less polluting chemicals such as, For reducing baths,

- Sodium sulfhydrate and alkali(soda or caustic)
- Sodium hydrosulphite and caustic soda.
- Sodium hydrosulphite in glucose/caustic.
- Glucose and caustic soda.
- Alkaline sodiumformaldehyde sulphoxylate.

For oxidation baths

- Hydrogen peroxide and liquid ammonia.
- Sodium perborate .
- Sodium bromate and acetic acid.
- Alkaline solution of sodium chlorite at pH 10.
- Air oxidation , wherever possible.

Use of Spent Dye Bath in Dyeing

A major consumption of the sulfur dyes is in the dyeing of black shades and a large amount of dye is used to produce a good black. Due high concentration of dye in the dyeing bath , al the dye is not transferred to the substrate and a large amount of dye is always remains unexhausted at the end of dyeing. Which if drained creates problem at water treatment plants and increase the cost of treatment. The unexhausted dye in these cases can be reused , after replenishing with

fresh dye, when repeated lots of a particular shades has to be produced (say black).

The dye liquor at the end of dyeing cycle is collected in the tanks made for this purpose, the volume is made up for the lost liquor in dyeing ,the dye which is to be replenished is separately and added to it. Similarly the quantities of the electrolytes , and reducing agents are calculated and replenished. This bath then can be used as a fresh dye liquor.

The spent dye bath reuse is recommended for the self shades and blacks only, and not in combination shades because, where a mixture of dyes is used the exhaustion properties of the dyes is different and it is not possible to replenish the bath, for producing the exact shade.