Sulfur Dyes

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Sulfur dyes are synthetic organic substantive dyes for cellulosics.

Chemical structure: The exact chemical structure of the 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. (read about sulphur dyes)

Properties of sulfur 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 vide 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 sulfur 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

Mechanism of the sulfur 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 compatible 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.

A typical dyeing cycle is as shown below
Here A = Wetting agent, Dye bath stabiliser, Sodium sulfide, Soda ash
B = Reduced dyes slow addition
C = common salt or Galuber salt
D = Oxidizing agent
E = Neutral Soap + soda ash
F = Dye fixer / softener / final chemical rinse

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.

4. 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 times 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. After washing the material is given a hot wash at 70°C.

5. 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.

6. Aftertreatment

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°C.

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,
   a. Soda ash wash 2-3 gpl
   b. Sodium Acetate 2-3 gpl
   c. Tetrasodium pyrophosphate 5.0 gpl
   d. 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, and insufficient washing after dyeing of unexhausted dyes and poor or insufficient soaping treatment. To get overall good fastness properties:
   a. 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.
   b. The color should be dissolved in sufficient quantity of water, by keeping in mind the maximum solubility of the dye.
   c. 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.
d. 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 dye or electrolyte, delay between dropping of bath and washing, oxidation step. Following are the corrective actions for correcting and avoiding the bronziness problem,
a. proper dissolution of the dyestuff.
b. Thorough washing and treatment with reducing agent before oxidation.
c. Use of surfactants, sequestering agents, dispersing agents, dye bath stabilizers, and anti oxidants in reducing bath.
d. Using sufficient and calculated quantity of reducing agents.
e. Using appropriate quantity of electrolyte e.g. less than 15 gpl.
f. After treatment with 2-3 gpl TR oil + 1-2 cc/ltr of ammonia in luke warm bath, to overcome the problem.
g. Treatment with soap solution at boiling temperature.
h. Using a blank bath of sodium sulphide.

3. Tendering
Tendering means the loss of strength or degradation of cellulolic 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
a. Leveling the dyed material by running in a blank bath containing excess sodium sulphide, dispersing agent, wetting agent at a temperature of 80-90 degrees, 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.
b. 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:-
Normally 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 precipitation. Generally naphthalenesulphonic acid –formaldehyde condensate, ligninsulphonates and sulphonated oils are used in sulphur dyeing.

Dyeing cycle of black dyeing in package form
Environmental problems and sulfur 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 sulphide 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:
1. Sodium sulfhydrate and alkali (soda or caustic)
2. Sodium hydrosulphite and caustic soda.
3. Sodium hydrosulphite in glucose/caustic.
4. Glucose and caustic soda.
5. Alkaline sodiumformaldehyde sulphone.

For oxidation baths:
1. Hydrogen peroxide and liquid ammonia.
2. Sodium perborate.
3. Sodium bromate and acetic acid.
5. Air oxidation, wherever possible.

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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 to high concentration of dye in the dyeing bath, all 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 shade 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.

Sulphur dyeing is used for dyeing of cotton and in market it is available in powder and liquid form also. In exhaust dyeing maximum powder form is used in dyeing of cotton material.

In sulphur black dye main advantages it can cover immature cotton available in fabric portion and get lot of fashion shade. Even in Fabric Dyeing general fashion is there if shade wise any major problem is there convert it sulphur black shade.

Here in this article we are going to show the sulphur dye used in different machinery.

**Drumming machine:** For garment micro garment quality was used (50% polyester and 50% cotton blend quality) one trail was observed in 50 kg lot.

Quality:- micro garment quality (50% polyester and 50% cotton blend quality)

Quantity:- 50 kg

M; L:- 1/15

M/c used:- Drumming m/c

Order:- For local quality.

Process used:

1) Desizing agent (Enzyme) = 200 gram
2) Lubricant = 500 gram
3) OT = 200 gram

(Run at 55 degree Celsius, 20 minute holding time.)---Washing------
II) Lubricant = 500 gram
Sulphur Black =4.500 kg
Sodium Sulphide=4.500 kg
Common Salt =10 kg
Soda ash =700 gram
(65-70 degree Celsius, holding time 30 minute)----Washing----

III) Hydrogen peroxide=700 gram
Acetic Acid=400 gram
(10 minute holding, cold)

IV) Bio-polishing:-
Bio-SL (Enzyme) =400 gram
Lubricant=500 gram
Acetic Acid=800 gram
(Holding time 30 minute, at 50 degree Celsius)----Washing----washing----unloading for finishing section.

Note: Acetic Acid quantity was taken more because water PH is alkaline coming range 8.0-8.5.

From above it was observed three processes was involved .Desize----sulphur dyeing---oxidation---bio-polishingwashing---washing .The above lot within 2 hours was taken out. Result was satisfactory for local quality within short time getting result.

Continuous Dyeing machine:
For Cotton Twill quality (Drill quality)
Order:-Export Quality.

I) Sulphur Black dye=95 gpl
Crypto-anionic wetting agent=2 gpl
Antimigrating agent=10 gpl
Padding----drying-----Chemical padding

II) Chemical Padding:-
Soda ash=20 gpl
Sodium Sulphide=95 gpl
Paddingsteamingcold wash-oxidation

III) Oxidation:-
Potassium dichromate=5 gpl
Acetic acid=2 gpl
(50-55 Degree Celsius)

IV) Soaping:-
    Soap=0.5 gpl
    Soda ash=0.5 gpl
    (85-90 Degree Celsius)--------hot washhot washcold washdrying.

Final process:-Dye Paddingdrying in hot flue drier---chemical padding---steamingcold washoxidationsoapinghot wash-hot wash cold washwashing and batching for finishing.

(For Fabric neutral PH if required slight acetic acid can be taken in last washing tank)

Jigger Dyeing machine:-

For Drill cotton Quality (For 100 kg lot).

Order:-Local Quality

I) Sulphur Black dye (Powder) =6-8%
    Sodium Sulphide=1.5 part of dye quantity.
    Common salt=10 kg
    Soda ash=2 kg

First Dye-2 Turn (Room Temp)

Sodium sulphide=2Turn (Room Temp) +4Turn (Boil)
    +
    Common salt=4Turn (Boil) (Salt Addition in two installment)
    +
    Soda ash=4Turn (Boil) (Soda Addition in two installment)

II) Oxidation:-
    Hydrogen Peroxide=2 gpl
    Acetic acid=1 gpl
    (50-55 degree Celsius, 4Turn running drain)

III) Soaping:-
    Soap:-0.5 gpl
    Soda ash=0.5 gpl
    (80-85 degree Celsius, 4turn running drain)

Hot wash2Turn---Hot wash=2Turn (Fresh water) ---cold washunloaded.

Final process: - Dye drain---cold wash---oxidation---soapinghot washwashcold washUnload.

Disclaimer:

"The information and recommendations presented here are compiled with the sole aim of understanding and cannot be extended to cover every possible case. They are intended to serve as non binding guidelines and are without prejudice and warranty."