

Dyeing applications of Sulphur dyes

Sulphur dyes

- Sulphur dyes are synthetic organic substantive dyes, produced by the thionation or sulphurisation of organic intermediates containing nitro or amino group
- They are like vat dyes, highly colored, water insoluble and have to be converted to water soluble, substantive form(leuco)before application to textile material.
- Sulphur Dyes are mainly used for dyeing cellulose fibers. Apart the cellulose fibers, these can be also used for dyeing staple fibers and yarn.

Sulphur dyes

- Sulfur dyes are used mainly for dyeing textile cellulosic materials or blends of cellulosic fibers (qv) with synthetic fibers such as acrylic fibers, polyamides (nylons), and polyesters. They are also used for silk (qv) and paper (qv) in limited quantities for specific applications. Solubilized sulfur dyes are used on certain types of leathers (qv). From an applications point of view, the sulfur dyes are between vat, direct, and fiber-reactive dyes.

Salient features

- They give good to Moderate lightfastness and
- Good wet fastness at Low cost and rapid processing
- Traditionally, these dyes are applied from a dyebath containing sodium sulfide.
- However, development in dyeing techniques and manufacture has led to the use of sodium sulfhydrate, sodium polysulfide, sodium dithionite, thiourea dioxide, and glucose as reducing agents.
- In the reduced state, the dyes have affinity for cellulose and are subsequently exhausted on the substrate with common salt or sodium sulfate and fixed by oxidation. The range of colors covers all hue classification groups except a true red. As a rule, the hues are dull compared with other dye classes. Black is the most important, followed by blues, olives, and browns

Method of use of Sulphur dyes

- The conversion is usually carried out by the treatment with aqueous sodium sulphide solution
- Since the leuco form has affinity for cellulosic fibre and since they are sensitive to atmospheric oxidation, they can be easily oxidised to the parent sulphur dye
- Thus they have to be dyed from the aqueous sodium sulphide solution

Classes of Sulphur dyes

- Three classes of Sulphur dyes:
 1. Conventional or water insoluble dyes
 2. Leuco Sulphur dyes
 3. Solubilized Sulphur dyes

Conventional Sulphur dyes

- Conventional Sulphur dyes are used by this method:
- These are insoluble or partly soluble in water. They have variable but slight affinity for the textile fabric
- Before dyeing the dyed are pasted with a little amount of cold water, the required amount of sodium sulphide is added and dissolved by adding water
- Boiling for about 10 mins completes the dissolution process
- This is then added to the dyebath with soda ash finally the material to be dyed is entered to the dyebath

Properties of Sulphur dyes

- From the name it is clear that these dyes contain little amount of sulphuric acid. The fibers those can be dyed by these dyes are Viscous, Staple fibers, Yarn, any materials which give a resin finish, silk etc. These dyes have an excellent light fastness properties.
- Dyeing temperature: 80-95 degree C (Optimum) but sometimes at cold temperature also.
- It is a good soluble in Na_2S .
- It has a good exhaustion.
- Its dyeing rate is moderate.
- It is a soluble in water.
- Make rapid black on cellulose materials.
- Sometimes create direct prints on cellulose.

Application of sulphur dyes

- Where boil fastness is not very important but a good wash is important of dull brown, khaki color clothes, sulphur Dyes are used. The most friendly sulphur dye among all the members of the sulphur acid dyes family sulphur Black. It shows affinity for linen and jute fibers. It works excellent with the black color and gives excellent color and light fastness.
- Sulphide Dyes are dyes from a dye bath containing common salts and Sodium Sulphide. This mixture is oxidized with some oxidizing agents in a fresh bath. The oxidizing agents are Sodium bichromate and Hydrogen Peroxide.
- These Dyes are used for ***Jigger, Winch*** and for package dyeing of Cotton and Viscose-rayon. These dyes are economically beneficial if used for continuous basic.

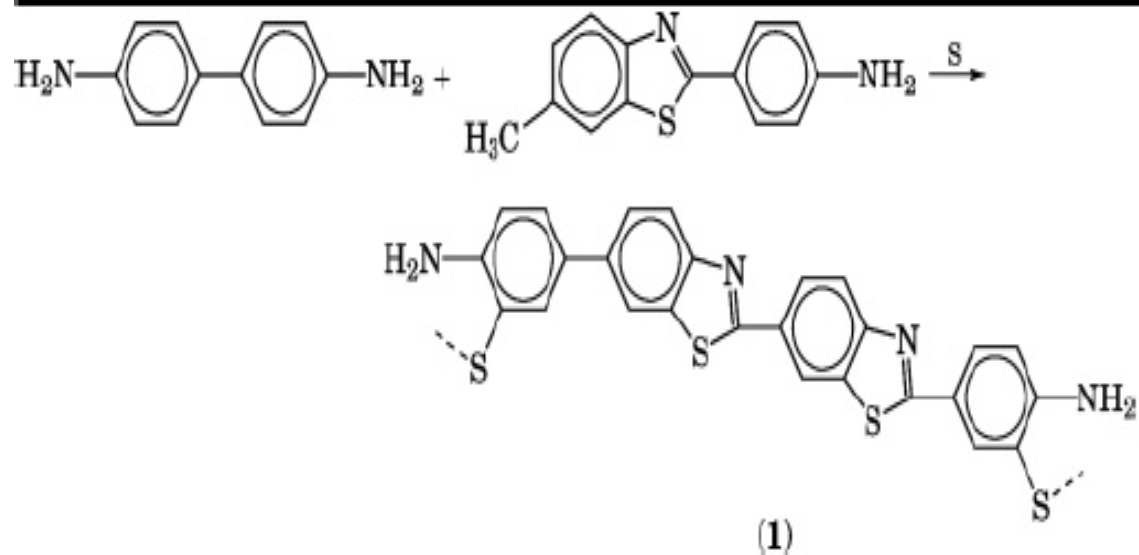
Sulphur

- The yellow, orange, and brown sulfur dyes belong to this group. The dyes are usually made from aromatic amines, diamines, and their acyl and nuclear alkyl derivatives. These may be used in admixture with nitroanilines and nitrophenols or aminophenols to give the desired shade. The color formed is said to be the result of the formation of the thiazole chromophore, evident in dye structure

Investigation into the structure of the sulfur bake dye Immedial Yellow GG, CI Sulfur Yellow 4 [1326-75-6] (CI 53160), by chemical degradation of the dye and confirmatory synthesis of the postulated structures showed that a mixture of four dyes was obtained when benzidine and 4-(6-methyl-2-benzothiazolyl)aniline were baked with sulfur. The original British patent for Sulfur Yellow 4 dates back to 1906 (19).

The principal structure obtained is

Immedial Yellow GG,CI Sulfur Yellow4



Manufacture of Sulphur bake

- Thionation of the various aromatic amino or nitro compounds with sulfur was formerly carried out in iron pan fitted with agitators and heated by gas fire. However, some bakes begin to stiffen up as the reaction progresses preventing further agitation; consequently, the baking process is not uniform throughout. Baking pans have been replaced by more efficient iron cylinder rotary bakers. The bakers, usually of 500–1000 kg capacity, are heated directly by gas jets or hot flue gases from a fire source and rotated at 2–10 rpm on hollow-end trunnions supported by self-aligning bearing rollers. The off-gases from the reaction are led through a catch pot to a scrubber unit containing caustic soda solution.
- S and NaHS for recycling. The bakers are rotated until the raw dye is ground to a powder. It is discharged and standardized to strength and shade purified by solution in either caustic soda or sodium sulfide. Insoluble matter is removed by filtration. The liquors are evaporated to dryness on a steam-heated rotating single- or double-drum dryer or the dye is precipitated by the addition of acid or sodium bisulfite or by blowing air into the alkaline brew. H_2S generated is absorbed in caustic soda solution. The precipitated product is filtered, washed, and air blown dry before discharge. The final drying is usually carried out in fan-assisted steam-heated air ovens

Application

- Sulfur dyes are applied to leuco form. In this form, the dye has affinity for the fiber. After the dye is completely absorbed by the fiber, it is reoxidized in situ
- In dyes, such as the bright blues which contain quinon imine groups, further reduction takes place in a manner similar to the reduction of the keto group in vat dyes. The sulfur dyes are classified according to application method and the structure of the intermediates, into ordinary or conventional dyes, leuco or prereduced dyes, and thiosulfonic derivatives of conventional dyes (solubilized sulfur dyes)

Reducing Agents used

The reducing agent traditionally employed with sulfur dyes is sodium sulfide, but sodium sulfhydrate, NaHS, together with a small quantity of alkali such as sodium carbonate or sodium hydroxide is also widely used.

The dyebaths prepared in this way are less alkaline than those with sodium sulfide alone which facilitates the rinsing of the dyed goods.

Effluent control has resulted in a search for alternative reducing agents.

Other reducing agents

Alkaline sodium dithionite(sodium hydrosulfite) can be used with some sulfur dyes, particularly the blues, but over-reduces red-browns such as CI Sulfur Brown 12 [1327-86-2], CI Sulfur Red 6[1327-85-1], and similar types. Alkaline sodium formaldehyde sulfoxylate has also been employed with blues, but has the same drawbacks.

Glucose and sodium hydroxide in almost boiling solution have been proposed for solubilized or dispersed sulfur dyes. Small amounts of sodium sulfide or sodium dithionite together with glucose and sodium hydroxide assist the reduction, but the pH should be maintained above 10.5 throughout the dyeing.

Dyeing of blends with Sulphur dyes

- Blends of polyester with cotton or viscose are first dyed with disperse dyes, then with sulfur dyes (see Fibers, polyester; Fibers, regenerated cellulosics). Disperse and sulfur dyes can also be applied simultaneously in a pad–dry–thermofix / chemical reduction pad–steam sequence.
- In this case, the sulfur dyes cannot be used in their reduced form because of the effect of the sodium sulfide on the disperse dye. Therefore, this method is confined to the solubilized sulfur dyes or sulfur dyes in the dispersed form. Solubilized sulfur dyes can also be applied without reducing agents. The dye, together with urea and thiourea or similar compounds, is padded on 100% cotton, then dried and thermo fixed at 150–175 degreeC.
- In the case of polyester–cotton, suitable disperse dyes can be added to the padding liquor and thermofixed at higher temperatures together with the solubilized sulfur dye. Other uses of finely dispersed sulfur dyes without reducing agents have been described

After treatments

Because the dye is applied by reduction and oxidation, many methods are available to obtain the correct hue. Air oxidation takes place gradually after the residual reducing agent has been rinsed away, but in general chemical oxidation is faster.

The traditional oxidizing agents include sodium or potassium bichromate mixed with acetic acid; addition of copper sulfate slightly improves lightfastness.

After Treatments

However, because of ecological restrictions on bichromates, other oxidizing agents are coming into use, such as hydrogen peroxide, sodiumperborate, and products based on potassium iodate or sodium bromate mixed with acetic acid.

Sodium chlorite is used in alkaline solution together with detergent. These reagents give different effects and are more suitable under some conditions than others. Generally speaking, hydrogen peroxide and sodium perborate give dyeings that are slightly less fast to wet processing than other products. Aftertreatments include resin finishes, which improve fastness properties, and dye-fixing agents of the epichlorhydrin–organic amine type. These agents react with the dye to give condensation products that are not water soluble and hence more difficult to remove.

Uses of Sulphur dyes

The sulfur dyes are widely used in piece dyeing of traditionally woven cotton goods such as drill and corduroy fabrics. The cellulosic portion of polyester–cotton and polyester–viscose blends is dyed with sulfur dyes.

Their fastness matches that of the disperse dyes on the polyester portion, especially when it is taken into account that these fabrics are generally given a resin finish. Yarn is dyed with sulfur dyes, although raw stock dyeing has declined in the 1990s.

Uses

- The dyeing of knitted fabrics, both 100% cotton or blends of cotton with synthetic fibers, is increasing. Although the problems of premature oxidation of the dyebath should not be underrated, sulfur dyes are successfully applied to this type of fabric on open and closed winches and on modern jet-dyeing machines . Piece dyeing on the jig uses considerable quantities of sulfur dyes. Conventional methods are used, but special care is necessary to ensure that the dyes are completely dissolved, preferably in a separate vessel, permitting the boiling of dye and reducing agent together