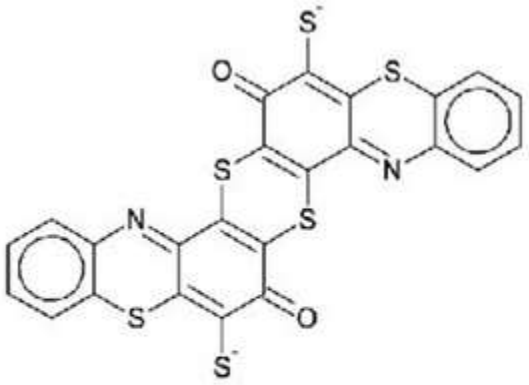
Sulphur Dyes



Sulfur Black I

Sulfur dyes are the most commonly used dyes **manufactured for cotton**. They are **inexpensive**, generally have **good wash-fastness**, and are **easy to apply**. Sulfur dyes are **predominantly black, brown, and dark blue**. **Red sulfur dyes are unknown**, although a pink or lighter scarlet color is available.

The sulphur dyes are named so because of **the presence of sulphur atoms** in their molecules. Like direct dyes, sulphur dyes are also **quite cheap** for dyeing cellulosic textiles with limited color fastness properties.

Sulfur linkages are the **integral part of chromophore** in sulfur dyes. They are organic compounds consisting of **sulfide (–S–), disulfide (–S–S–)** and **polysulfide (–Sn–)** links in **heterocyclic rings**. They feature **thiazoles, thiazone, thianthrene**, and **phenothiazonethioanthrone** subunits. Being **nonionic**, sulfur dyes are **insoluble** in water.

Properties of Sulphur Dyes

1. Sulphur dyes have **Sulphur linkage** within their molecules.
2. Sulphur dyes are water **insoluble dyes**.
3. To increase the **substantivity** of this dye they are to be converted in to **soluble leuco** form by treating them **with reducing agent**.

4. Sulphur dyes have **moderate to good light fastness** with rating about 4. This light fastness **may be improved** by an **after treatment with metallic salt.**
5. These dyes have **fair to good wash fastness** with rating about 3-4. This good wash fastness is due to its **larger molecular size & insolubility in water**.
6. They are **not applicable to wool** due to strong alkaline condition.

Classification of Sulphur Dyes

Sulphur dyes are classified based on **chemical structure** and **application**.

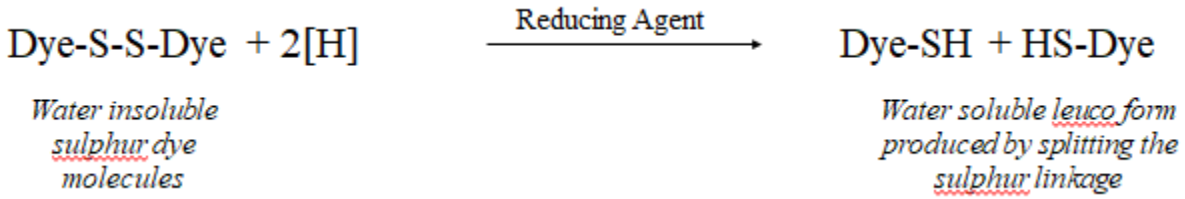
- **Chemical classification** includes two types, **sulphur dyes and sulphurised vat dyes.**

i) Sulphur dyes include **only sulphur linkages** and are **reduced with Na_2S** at boil.

ii) Sulphurised vat dyes **retain both sulphur linkage as well as carbonyl group as chromophore** and are **reduced with $Na_2S_2O_4$ and NaOH combination** at specific temperature but **cannot be reduced** with Na_2S.

Mechanism of Sulphur Dyes

- ✓ The Sulphur dyes **contain Sulphur linkage** within their molecules.
- ✓ They are **insoluble in water** but can be made soluble in water by **treating them with reducing agents.**
- ✓ This also makes them **substantive** towards cellulosic fibres.
- ✓ Na_2S acts as reducing agent that breaks the Sulphur linkage and break down the longer molecules in to simple components which can penetrate the material (fiber/fabric) surface easily.



- ✓ This thios containing the –SH groups are readily oxidized by the action of **atmospheric O_2** or any other **oxidizing agents (eg. $Na_2Cr_2O_7$).**

- ✓ This reconverts the water **soluble leuco form** of Sulphur dye into previous water insoluble form which has a **very good wash fastness** property.
- ✓ Sulphur dyes are **negatively ionized**. Addition of salt improves efficiency of dyeing by increasing physical force.
- ✓ Oxidizing is occurred as like ----

$$Na_2Cr_2O_7 + 8CH_3COOH \longrightarrow 2CH_3COONa + 2\,(CH_3COO)_3Cr + 4H_2O + 3[O]$$

$$\text{Dye-SH} + \text{HS-Dye} + [O] \xrightarrow{\text{Oxidizing Agent}} \text{Dye-S-S-Dye} + H_2O$$

*Sulphur dyes are negatively ionized. Addition of salt improves efficiency of dyeing by increasing physical force

Reducing Step of Sulphur Dyes

Reducing step is the most important in the application of sulphur dyes. Unless the dyes are converted into the completely soluble form, the full color value cannot be achieved. The solubility of reduced sulphur dyes varies appreciably from dye to dyes. The reducing agents used for sulphur dyes are:

1) Na-Sulphide (Na_2S)
2) Na-Hydro Sulphide (NaSH)
3) Thioglycolic Acid ($HS\text{-}CH_2\text{-}COOH$)

- ❖ But, Na Sulphide is the most widely used reducing agent for dissolving sulphur dyes. These may be replaced by Na-Hydrosulphide in some cases.
- ❖ Again, over reducing of the dye may take place, leading to a product having lower affinity for cellulosic fibres.
- ❖ Hence lower color yields are obtained along with wastage of dyestuff.
- ❖ In some cases lower wash fastness results if Na-Hydrosulphide is used.
- ❖ It also decreases the life time of the vessel.

Dyeing Steps of Sulphur Dyes

- ➢ Once reduction and solubilisation is over, wet cotton is dyed at 90–95°C for 30–60 min after which salt is added and dyeing is continued for further 1.5–2 h; the bath is drained out and dyed cellulose is washed thoroughly.

- Due to the presence of large amounts of dye required to produce deep shades and its moderate affinity for cellulose, dyeing time before and after salt addition should be kept on the higher side to promote exhaustion of bath.
- Reduction as well as dyeing of cotton is preferably carried out in jigger or winch.
- At least four turns are imparted in dye bath after which salt is added and further eight turns are imparted at boil.
- The bath is dropped, dyed cotton is cold washed for 2 turns, oxidized for 2–4 turns followed by soaping, washing and padding with CH_3COONa.

Oxidation Step of Sulphur Dyes

After dyeing the reduced water soluble form of the dyes have to be converted in to the original water insoluble form by oxidation.
The commonly used oxidizing agents are-
1) Potassium dichromate ($K_2Cr_2O_7$)
2) Na-Perborate ($Na_2H_4B_2O_8$)
3) Na-per carbonate ($NaHCO_3$)
4) Na-peroxide (Na_2O_2)

The method of oxidizing agent selection plays an important role in the development of correct shades & their optimum fastness properties. Using of different oxidizing agents may give the following results-
1) Use of perborate or per carbonate in presence of acetic acid gives brighter shade.
2) Treating dyed material with dichromate without rinsing reduces color losses and causes dull shade.

Defects of Sulphur Dyeing

1) Bronziness or Dullness of shades:

Causes:

1. Excessive delay between lifting of the material from the dye bath and washing off.
2. The presence of excessive dyestuff on the material.
3. Insufficient Na_2S (i.e. reducing agent) in dye bath.
4. Exposure of goods to air while dyeing.
5. Excessive heat.

Remedies:

1. Good washing and dilute solution of Na_2S (0.1%) at 30°C or,
2. A treatment with boiling soap solution or a strong Na_2S solution or,
3. A treatment with a solution containing 10% saponified palm oil at 60°C

2) Sulphur black Tendering:

Causes:

1. Gradual oxidation of Sulphur to H_2SO_4 on storage.
2. After treatment with copper salts causes rapid tendering.
3. Presence of iron as an impurity causes rapid tendering.
4. The method of oxidation for the reconversion to insoluble form influence tendering.

Remedies:

1. Treatment of dyed material with 1-3% of $K_2Cr_2O_7$ and 1-3% of CH_3COOH at 60°C temperature for 30 minutes followed by through rinsing.
2. Treatment with a little CH_3COOH so that H_2SO_4 may be converted in to harmless acetic acid.

Stripping of Sulphur dyes

- ✓ Unevenly dyed shades on cellulosic materials with sulphur dyes may be corrected by a treatment with a **warm solution of Na_2S** in the presence of **polyvinyl pyrolodine.**
- ✓ If this method is found to be **ineffective** then the uneven dyed material may be treated with a solution of a **NaOCl or bleaching powder (2-3 gm/litre of available chlorine).**

- ✓ In some cases bleaching with **KMnO4** solution may be effectively carried out. In other cases the dyed material may be treated with warm **NaOC**l solution in the presence of **NaOH**.
- ✓ The uneven dyeing of material causes due to the following reasons:

i) The oxidation of dye during dyeing when the material comes in contact with air.
ii) Presence of gummy material on the fabric.
iii) Defective Dye.

❑ Comparison between Sulphur and Vat Dyes:

Criteria	Sulphur Dye	Vat Dye
Molecular Size	Dye molecules are very Large	Smaller than Sulphur
Shade	Gives dull shade due to varying conditions	Gives bright shades
Fabric Dyed	Cotton, Rayon, Nylon & P/C	Cellulose, Rayon etc
Hydrolysis	Under high temperature and Humidity	Susceptible to hydrolysis i.e. easy to Hydrolysis.
Wash Fastness	Good to very good	Excellent
Price	Cheaper than Vat dye	Very costly dye
Light fastness	Good to very good	Excellent for anthraquinone.
Sulphur linkage	Contain Sulphur linkage	No Sulphur linkage is present.
Ionization	The dye molecules are negatively ionized after reduction	Similar to sulphur dye.