

Chapter 4: Sulfur Dyes and Their Application

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However you care to look at them, sulfur dyes are extraordinary. No-where else is there a class of dyes which delivers so much color for your money, with products whose chemical structures are, in almost all cases, unknown. No-where is there a class of dyes with such good fastness to washing, coupled with such sensitivity to treatment with chlorine. Some are notorious for a characteristic mercaptan odor during dyeing, but no one selling other dyes for cellulosic fibers regards them as anything but serious competition. There is no black on cellulose which can compare with the attractive shade and depth possible with C.I. Sulfur Black 1, which accounts for it being one of the most widely used dyes in the world.

Because many sulfur dyes are sold in the form of pre-reduced liquids, it is hard to make accurate comparisons with other dye classes on the basis of the weight of dye sold, but worldwide, sulfur dyes are certainly up there with acid, disperse and direct dyes.

In the 1860s a number of chemists had already observed the colors formed when certain organic nitro compounds were reacted with alkaline sulfides, but it was

not until a decade later, in 1873, that Croissant and Bretonniere produced a commercial brown dye from sawdust and bran, by heating them with alkaline sulfides. This first sulfur dye was known as Cachou de Laval and in the right conditions it could be exhausted onto cotton. The component of sawdust and bran responsible for the color is lignin. Today, C.I. Sulfur Brown 1 is still being made from lignin sulfonates, which are the dark colored by-products formed when sulfite bleaching wood pulp for paper making.

Many of the sulfur dyes used today start from well defined chemical intermediates, and it is the structures of these intermediates which appear in the Colour Index (1) to confuse the unwary.

In fact, these intermediates are treated in one of two main ways to form the ill-defined structures known as sulfur dyes. The first is to bake the organic material, or intermediates, with sulfur, with or without sodium sulfide, Na₂S. The second is to boil the intermediates with sodium polysulfides, in aqueous or alcoholic solvents, under reflux conditions.

The General Nature of Sulfur Dyes

When first thinking about sulfur dyes it is convenient to emphasize their similarity to vat dyes. They are intrinsically insoluble, but they dissolve in solutions of alkaline reducing agents (usually sodium sulfides) from which they are substantive to cellulosic materials. Once on the fiber, they are converted back to their original pigmentary form by oxidation.

When this preliminary information has been digested, it is the distinctive differences between the two dye classes which will seem more important.

Finally, it will become apparent that the differences between the two classes are bridged by a group of dyes known as sulfurized vat dyes, which are not classified separately in the Color Index (2) but which have some characteristics of both

dye categories; for example, C.I. Vat Blue 43, C.I. Vat Green 7, C.I. Sulfur Red 10 and C.I. Sulfur Black 11 (3).

Functional Groups

The processes used for the manufacture of sulfur dyes ensure that sulfur has been introduced into the organic, aromatic ring structures of the intermediates. In its simplest possible form, the functional structure of a sulfur dye can be represented by the formula:



Such a formula shows two chromophores (or color bearing groups), indicated by the words Dye, joined together by two sulfur atoms, represented by -S-S-, and known as a disulfide linkage.

The two chromophores linked together hint that the molecule might be large and that it has no obvious solubilizing groups. In fact, like vat dyes, sulfur dyes are insoluble and pigmentary unless reduced.

Fig. 1 represents what happens when alkaline reducing agents are added to the insoluble sulfur color, Fig. 1a. The disulfide link splits in two, forming two leuco anions each accompanied by a sodium cation, $\text{Dye-S}^- \text{Na}^+$. These ions are known as mercaptides (or thiolates) and are soluble in water, Fig. 1b.

Like vat dyes, the water soluble sodium salt of the leuco-sulfur dye can be restored to its original pigmentary form by acid oxidation. It can also be converted into the insoluble acid-leuco form, called a mercaptan (or thiol), Fig. 1c, by the addition of acid; but do not ever add acid to reduced liquid sulfur dyes; see later.

Unlike vat dyes, reduction causes the sulfur pigment molecule to break apart at disulfide linkages, whereas all the peripheral changes in vat dye molecules leave the main structure intact.

There are other complications. The part of the molecule represented by Dye in Fig. 1 may also be reducible and depending on

ABSTRACT

Part 1 of this chapter covers the chemical development of sulfur dyes and the general principles of their application to cotton. Sulfur dye reduction and oxidation are compared with those of vat dyes. The effect of different chemicals on each part of the dyeing process is discussed with respect to their cost, benefits and environmental impact.

KEY TERMS

- Alkylating Agents
- Dyes
- Dyeing
- Functional Groups
- Leuco-Sulfur Anions
- Oxidizing Agents
- Pigments
- Reducing Agents
- Sulfur Dyes

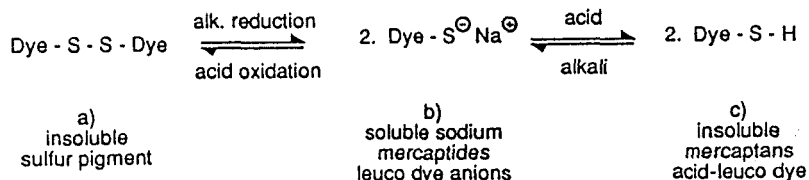


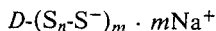
Fig. 1. Sulfur dye functional groups and their dyeing reactions.

Sulfur Dyes

the choice of reducing agent, over-reduction may result in irreversible changes (see next section).

If there are two or more mercaptide groups on the leuco-sulfur dye anion, oxidation will result in a polymeric or a crosslinked pigmentary molecule unlike the neat double molecule shown in Fig. 1a. Such products will not crystallize on soaping, cf. vat dyes, and will have pendant mercaptan groups present which could not find an adjacent group with which to form a disulfide link. These pendant groups may be quite reactive.

Finally, sulfur has a habit of forming chains of up to about six sulfur atoms in a row. Picturing the linkages as disulfides is certainly too simple. A more acceptable general formula for a reduced sulfur dye would be:



Here D is a chromophore or reduced chromophore, n is zero to five and m is greater than or equal to one.

Reducing Agents

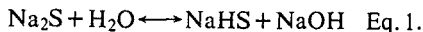
Worldwide, sulfur dyes are sold in a variety of forms, which include powders, dispersed powders, dispersed pastes, pre-reduced liquids and the liquid or powder forms of solubilized sulfur dyes which have been chemically converted to the sodium salts of thiosulfuric acids. These will all be more fully covered in the section on commercial products. But the various forms of dyes contain differing amounts and types of alkali and reducing agents as sold, which makes any general recommendation of the amounts to use for dyeing quite unreliable.

At this time, dyers in the U.S. are fortunate that almost all sulfur dyes available to them are either pre-reduced liquids or, in the case of sulfurized vat dyes, in the form of pastes.

Sulfide Reducing Agents

Sulfide reducing agents can be sodium sulfide (Na_2S), sodium hydrosulfide ($NaHS$), and sodium polysulfide (Na_2S_x , where x can be from one to six) which is sold primarily under a trade name as an aqueous solution. With regard to the first two, they are both available in a variety of strengths, both in solid and liquid form. It is important to always express the concentrations required in the same terms; i.e., as 100% active product. But the sulfide and hydrosulfide are chemically interrelated. In water, sodium sulfide is almost completely hydrolyzed to sodium hydrosulfide

and sodium hydroxide:



The equation is written with the equilibrium arrows indicating that the reaction can go either way. In fact, sodium sulfide solutions have pHs only about 0.1-0.2 units lower than solutions of the equivalent amount of sodium hydroxide, which means the reaction goes about 70% to the right. The equivalent ratios of 100% sodium sulfide, sodium hydrosulfide and caustic soda (sodium hydroxide) are about 10:7:5, which corresponds with the ratio of their molecular weights (78:56:40). In practice, this means that seven parts of 100% sodium hydrosulfide plus five parts of 100% caustic soda can be substituted for ten parts of sodium sulfide, but ten parts of 100% sodium carbonate (soda ash) are often substituted for the five parts of caustic soda. ~~which increases activity~~

Sodium sulfide has the remarkable ability to react with up to twice its weight of sulfur, to give mixtures of sodium polysulfides with the general formula Na_2S_x , where $x =$ one to six and is an average value for a particular product. In solution all possible S_x^- ions (S^- , S_2^- , S_3^- , . . . S_6^-) are in equilibrium not only with one another but with sodium hydrosulfite as well, cf. Eq. 1. The principle effect is that as the average value of x increases, the amount of hydrosulfite and its accompanying caustic soda are both diminished, resulting in a lower pH. At chemically equivalent concentrations, solutions of sodium sulfide (8 grams per liter) and sodium tetrasulfide (17 grams per liter) have pHs of 12.2 and 11.6 respectively, while at 8 grams per liter sodium tetrasulfide has a pH of 11.4. Polysulfides act not only as pH buffers but also as antioxidants.

Caustic and Hydro

Caustic and hydro, more properly called sodium hydroxide and sodium dithionite ($NaOH/Na_2S_2O_4$), are the conventional chemicals for vat dye reduction (Chapter 3), but this combination gives mixed and unreliable results with sulfur dyes as a whole. This is probably because the chromophores themselves are sensitive to over-reduction at the high reduction potentials delivered by this more powerful reducing system.

For those sulfur dyes referred to as sulfurized vat dyes—e.g., C.I. Vat Blue 43 and C.I. Vat Black 11—the combination works well, while sulfide reductions are generally not suitable. Sulfurized vat dyes are usually sold as pastes or powders and in their reduction behavior they resemble vat dyes quite closely. However, for most of the important sulfur liquid blues, navies and blacks, the color yield is very considerably diminished by caustic and hydro reduction, as is also the case for many of the sulfur liquid browns and red-browns.

One dye, C.I. Sulfur Red 14, is a marked exception, for the color yield is increased several fold by the use of caustic and hydro. But this dye is a nonconformist. It is a true red, has a known synthesized structure, has a relatively high price, and its purpose is to complement rather than underpin a range of sulfur dyes.

Alternative Reducing Agents

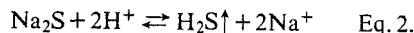
Several factors in the U.S. have contributed to the increased need for alternative reducing agents for sulfur liquid dyes. These include:

- The contraction in what was traditionally the principal market for sulfur liquid dyes, continuous dyeing. The number of continuous thermosol pad-steam dye ranges in use has fallen over the last ten years from about 144 to less than 120.

- The correspondingly rapid growth in the use of sulfur dyes in jet dyeing machines, as well as for dyeing warps on the ranges conventionally reserved for indigo.

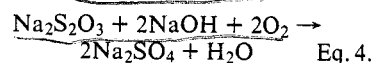
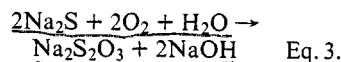
- The growing public concern for the environment.

Whenever the exhaust baths from the use of sulfur dyes are run to drain, they will contain sulfides. Sulfides in the presence of acids alone produce hydrogen sulfide, Eq. 2. This gas is sparingly soluble in water, smells of rotten eggs at extremely low concentrations in the air, and at higher concentration is odorless and life threatening.



The vertical arrow indicates the gaseous nature of hydrogen sulfide. Eq. 2 makes it clear that the source of the hydrogen ion, H^+ , is unimportant. The story can be different if excess of oxidizing agent is present in the acid solution.

In the generally larger continuous dyeing plants, the reducing effluents from the earlier stages of the dyeing are at least partially neutralized by combination with the oxidizing effluents from the later stages of the same dyeing. Both are held in treatment ponds, hopefully under controlled pH conditions, while aeration can take care of oxidizing the sulfides (S^{2-}) to thiosulfates ($S_2O_3^{2-}$) and sulfates (SO_4^{2-}), Eqs. 3 and 4. For further discussion of this and other aspects of sulfur dye effluent, see reference (4).



With smaller dyehouses, particularly those within urban areas, it is less certain that the treatment of sulfidinous wastewater is always appropriate. Batch liquors certainly can be collected, combined and treated in a relatively confined space, with either hydrogen peroxide or sodium hypochlorite as the oxidant. But not all

dyehouses are set up to hold and combine oxidizing and reducing effluent, and the town sewer may be the periodic recipient of sulfides.

As of this writing, a major sulfur dye producer has already introduced a black sulfur dye and is preparing to introduce others with considerably reduced sulfides, to be applied using a proprietary reducing agent. Not only will use of this agent minimize the problem of sulfides in poorly treated effluent, but because it is not very effective cold, it will also ensure that the highly substantive anionic leuco-dye will be generated gradually in batch dyeing as the dyebath temperature is raised. This could result in more uniform dyeings (5).

Glucose in the presence of alkali, usually caustic soda or a caustic soda/soda-ash mixture, has been used as another possible sulfur dye reducing agent. It also is activated at high temperatures, 90-95C (195-205F), and has met with some success, but it is not widely used in the U.S. at this time.

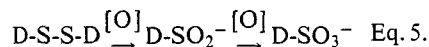
The ultimate outcome of the present activity in the area of new reducing systems for sulfur dyes is unclear; a situation paralleled by sulfur dye oxidizing systems 20 years ago.

Oxidizing Agents

The chemistries of applying sulfur and vat dyes run parallel in general concept. Pigmentary materials are reduced to water soluble substantive anions, dyed onto cellulose and then oxidized. However, the preferred reducing agents for sulfur dyes are not generally those used for vat dyes, which are too powerful for all but a few, notably the sulfurized vat dyes. A similar situation is duplicated in the choice of oxidants for sulfur dyes.

Peroxides and Percarbonates

The per-compounds are very economical and are widely used for vat dye oxidation. But, although these oxidants may be used for some sulfur shades, they have several drawbacks: they barely oxidize the sulfur red-browns and they can over-oxidize the sulfur blues. This over-oxidation is probably due to attack on the disulfide linkage to form water solubilizing sulfinate and sulfonate groups, and gives a reduction in wetfastness of about one point on the gray scale for staining adjacent fabrics:



where [O] stands for the per-oxidizing species. When used to oxidize the important sulfur blacks, the result is a bluer, lighter shade with poorer wetfastness.

It is particularly unfortunate that hydrogen peroxide (H₂O₂) gives such variable results with sulfur dyes, for environmentally it is beyond reproach. During oxidation reactions it gives up one of its oxygen atoms to become water.

Chrome and Acid

Worldwide, the standard oxidant for sulfur dyes has long been sodium bichromate (Na₂Cr₂O₇), known simply as chrome and normally used with acetic acid. An optional post-oxidative treatment with copper sulfate (CuSO₄) improves the relatively poor lightfastness of the yellow-brown sulfur colors, but the effect is lost on washing. The standards of wash- and lightfastness achieved with chrome and acid are those against which all alternative oxidants have been judged.

However, the presence of heavy metals salts in effluent has long been recognized as environmentally undesirable. The U.S. textile industry moved to alternative sulfur dye oxidants in the 1970s. Many other countries have still not moved. This raises a difficult philosophical question, which is being asked and answered by top management in the chemical manufacturing and using industries all over the developed world. What will be the short and long term effects of eliminating all known or potential environmental hazards from products while running the real risk of increasing their cost? The only time there is an easy answer is the rare occasion when there are no costs involved in making changes; otherwise there are only more and more difficult questions.

Sodium Bromate

In the U.S., formulations containing sodium bromate (NaBrO₃) have ousted most of the other alternative sulfur dye oxidants. The formulations require small amounts of sodium metavanadate as an oxidation catalyst, for bromate alone will certainly not oxidize the difficult sulfur red-browns.

The normally expensive catalyst can be prepared economically, in-situ, during bromate manufacture, and sodium nitrite is also included in formulated products to minimize the corrosion of stainless steel vessels.

Bromate oxidants are used at about 60C (140F) in solutions of one to two grams per liter for batch processing and five to ten grams per liter for continuous processing with the addition of similar amounts of acetic acid, to maintain a pH of about 4. Across the board, they produce sulfur dyeings of shade and fastness properties close to those obtainable earlier with chrome and acetic acid. There is only one other available oxidant for which this can be said.

Potassium Iodate

Potassium iodate formed the first very acceptable interim replacement for chrome and acid. However, iodine compounds have become very expensive, and the presence of iodine, which may be formed during processing, leads to problems of corrosion and with the effluent.

Remaining Alternatives

For most practical purposes one can say that there are no generally suitable alternatives for the bromate oxidation available in the U.S. today. Hypochlorites and the related chloramines can do the job, but are hard to control, and the amount necessary to steer between under- and over-oxidation varies from the red-browns on the one hand to sulfur black on the other.

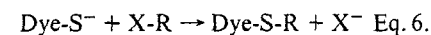
Sodium chlorite also falls short in a number of respects, including failure to oxidize red-browns. Sodium metanitrobenzene sulfonate (the alternative vat dye oxidant) may be effective, but has not attracted much interest.

Miscellaneous

Besides oxidants and reducing agents, there are a number of chemicals which can influence either the dyeing behavior or the fastness properties of sulfur dyes.

Alkylating Agents

When the reduced form of a sulfur dye is treated with an alkylating agent, the thiolate ion loses its electron and is, technically speaking, oxidized. Consequently, conventional oxidation may be avoided. The alkylation reaction can be illustrated by the simplified general equation:



where Dye-S⁻ is the reduced dye anion, X-R is the alkylating agent, Dye-S-R is the alkylated product and X⁻ is the leaving group.

If the organic group, -R, has a sufficiently high molecular weight, or if it has more than one leaving group and can join (crosslink) two or more dye anions, then the alkylated product can have extremely good fastness to severe washing.

But the chromophoric part of the reduced sulfur dye may require to be conventionally oxidized to develop its true color, in addition to the alkylation; e.g., C.I. Sulfur Blue 7. Frequently alkylation impairs lightfastness.

Because of the doubtful relationship between added costs and benefits, alkylating agents have not been widely accepted in the U.S.

Chelating Agents

If the supply of plant water has too high levels of calcium or magnesium hardness, chelating (sequestering) agents may be necessary. This is true not only for dyeing sulfur dyes, but, as stated earlier in Chapters 2 and 3, whenever anionic dyes are being used. All dye anions tend to react with multiply charged metallic ions—e.g., Ca⁺⁺, Mg⁺⁺, Fe⁺⁺⁺—to form insoluble or sparingly soluble salts. In the case of sulfur dyes, these salts are filtered out at the fiber surfaces and can result in dyeings with poor crockfastness (4, 6) or resistance to rubbing. Careful use of EDTA (ethyl-

enediaminetetraacetic acid) salts is recommended to take care of the problem.

Penetrants/Wetting Agents

Whenever dyes of high substantivity are being used, it is important that the dye liquor rapidly and completely wets out the goods being dyed. Anionic surface active agents (surfactants), such as salts of phosphated ethylhexanol, do a good job. However, there are many other surfactants which are good wetting agents, but which are totally unsuitable for use with sulfur dyes.

Beware of nonionic surfactants! They can interact with sulfur dye thiolates to form stable, soluble complexes with virtually no substantivity. They are also quite widely used in various auxiliary products (formulations) whose principle function may not be wetting. Any of these should be evaluated before using them in dyebaths with sulfur dyes.

Polysulfides/Rinsing/Soaping

Polysulfides, rinsing and soaping can contribute to achieving dyeings free from bronziness—a surface appearance resembling a metallic luster—characteristic of poorly dyed, heavy sulfur navy, blue or black shades. They can also contribute to good fastness to rubbing and crocking.

Polysulfide works by improving the stability of reduced dyebaths toward premature oxidation. Good rinsing prior to oxidation ensures the absence of a high surface concentration of sulfur dye, known as loose color. Soaping-off heavy shades after oxidation not only removes any oxidized surface color but also improves the shade stability towards changes on washing. Unlike vat dyes, there is no recrystallization of pigmentary sulfur dye particles within the fiber during soaping.

Salts

For those who have followed the progress

of direct and leuco-vat dye anions and their substantivity for cellulose in the preceding chapters, it should now be clear that increased salt concentration increases the substantivity of color bearing anions for the nonionic cellulosic fibers, when all other conditions are kept constant.

Leuco-Sulfur Dye Anions in Solution

Because of the uncertain chemical structure of most sulfur and leuco-sulfur dyes, there have been few studies of their dyeing properties which follow the classical physico-chemical experimental models. One important exception will be discussed later, under the subheading padding.

Clearly, sulfur dyes as a class have adequate solubility in the reduced form, otherwise they could not be sold as pre-reduced liquids. Equally clearly, a sorption isotherm of the Freundlich type would seem to pertain, since sulfur dyeings can be built to extremely heavy shades with no saturation value apparent. Properties such as bronziness and diminished crock or rubbing fastness begin to occur when the depth of shade exceeds the practical upper limit for individual dyes, but this does not mean that a saturation value has been reached.

The substantivity of reduced sulfur dyes is high partly because of the high concentration of salts in the reducing baths, but, parallel to direct and leuco vat-dye anions, this substantivity varies from dye to dye and can always be increased by the addition of common salt or sodium sulfate. Reduced sulfur liquids generally dye so rapidly that their addition is made gradually and at low temperatures.

As might have been predicted, the highly substantive leuco-sulfur dyes are not very readily stripped with reducing agents (which are salts), but a significant percentage of the dye can be removed (10-20%) in a bath of five to ten grams per liter of sodium sulfide, and more will be removed in a fresh reducing bath. This indicates that the sulfur dyeing process is a normal reversible equilibrium with the balance shifted heavily in favor of the dye on the fiber.

Review

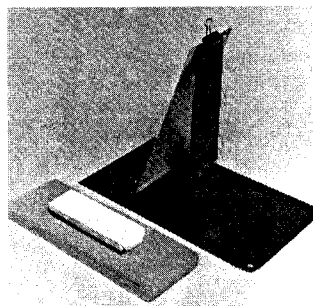
Sulfur dyes are pigmentary in nature, are mostly of unknown structure and dissolve in alkaline reducing agents to give the sodium salts of the leuco-dyes. After the leuco-dye anions have been sorped onto the cellulose and have diffused into it, they can be re-oxidized, in situ, leaving insoluble pigments entrapped in the cellulosic substrate. This gives many sulfur dyes a superficial similarity to vat dyes, however, some are more similar than others.

The hybrid colors known as sulfurized vat dyes, whose manufacture resembles that of sulfur dyes, are relatively hard to reduce and are not generally sold as pre-reduced liquids but rather as pastes or powders. They are easily re-oxidized when in the leuco form. On the other end of the scale, most sulfur colors are easy to reduce (sodium sulfide solutions have a relatively low reduction potential) but few are fully redeveloped by air oxidation and powerful oxidizing systems are required, particularly for the red-brown shades; e.g., C.I. Sulfur Red 10. The resistance of the leuco dyes to oxidation, and the much greater stability of sodium sulfide and polysulfide solutions towards air oxidation, compared with alkaline sodium hydrosulfite, are the reasons sulfur dyes can be sold as pre-reduced liquids and why it is possible to store them in the reduced state.

It took an American entrepreneur to fully appreciate the market value of the pre-reduced sulfur liquid concept, in 1936. The result has made pre-reduced liquids the standard form of sulfur dyes in the U.S. today. ☺

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Problems With Static?

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