Kirk-Othmer Encyclopedia of Chemical Technology.

SULFUR 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. They give good to moderate lightfastness and good wetfastness at low cost and rapid processing (see Dyes, application and evaluation).

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 (qv) 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 (see Dyes and dye intermediates).

The first sulfur dyes were produced in 1873 by heating organic cellulose-containing material, such as wood sawdust, humus, bran, cotton waste, and waste paper, with alkali sulfides and polysulfide (1). These dyes were dark and hygroscopic and had a bad odor. Composition varied and they were easily soluble in water giving greenish dyeings, both from alkali and alkali sulfide baths. The dyes were fixed on cotton (qv) fiber and eventually turned brown on exposure to air or chemical oxidation with bichromate solution. The valuable tinctorial properties of these dyes, in addition to their low price, led to their use in the cotton dyeing industry. They were sold under the name of *Cachou de Laval*. The main constituent was lignin (qv), which is used to produce CI Sulfur Brown 1.

The quality of sulfur dyes has greatly improved, mainly because well-defined organic compounds are used as starting materials. Owing to better techniques, sulfur dyes have good storage stability and fastness properties, and are generally easily adaptable to modern dyeing methods. An overview of the development of sulfur dyes is given in Table 1. In the 1980s and 1990s, reduction of sulfide levels has been achieved.

1. Chemical Properties

1.1. Classification and Structure

Little is known about the structure of sulfur dyes, and therefore, they are classified according to the chemical structure of the starting materials.

The process of sulfurization is usually carried out by a sulfur bake, in which the dry organic starting material is heated with sulfur between 160 and 320°C; a polysulfide bake, which includes sodium sulfide; a polysulfide melt, in which aqueous sodium polysulfide and the organic starting material are heated under reflux or under pressure in a closed vessel; or a solvent melt, in which butanol, Cellosolve, or dioxitol are used alone or together with water. In the last two methods, hydrotropes may be added to enhance the solubility of the starting material. The hydrotropes improve yield and quality of the final dyestuff.

The temperature and duration of heating have a marked effect on both the shade and properties of the dye and conditions have to be carefully controlled in order to achieve uniformity. The precipitation by air oxidation must also be controlled to prevent variations in shade.

Table 1. Historical Events in the Development of Sulfur Dyes

Year	Development	Product	CI designation		CAS Registry	Ref.
			Name	Number	Number	
1873	heating organic wastes with alkali sulfides/alkali polysulfides	*Cachou de Laval*	Sulfur Brown 1	CI 53000	[1326-37-0]	1
1893	heating benzene and naphthalene derivatives with alkali polysulfides	Vidal Black	Sulfur Black 3	CI 53180	[1326-81-4]	2
1897	sulfurization of diphenylamine derivatives	Immedial Black V	Sulfur Black 9	CI 53230	[1326-97-2]	3
1899	inexpensive black from 2,4-dinitro-phenol by use of reflux method of sulfurization	Sulfur Black T	Sulfur Black 1	CI 53185	[1326-82-5]	4
1900	use of leucoindophenols	Immedial Pure Blue	Sulfur Blue 9	CI 53430	[1327-56-6]	5
	first reddish (bordeaux) dyes from 8-amino-2-hydroxyphenazine	Immedial Maroon B	Sulfur Red 3	CI 53710	[1327-84-0]	6
1902	commercial orange and yellow dyes from toluene-2,4-diamine	Immedial Orange C	Sulfur Orange 1	CI 53050	[1326-49-4]	7
1904	clear green dye from phenyl-peri acid indophenol	Thionol Brilliant Green GG	Sulfur Green 3	CI 53570	[1327-73-7]	8
1908–1909	chlorine fast blue dyes from carbazole and *N*-ethylcarbazole indophenols	Hydron Blue R	Vat Blue 43	CI 53630	[1327-79-4]	9
		Hydron Blue G	Vat Blue 42	CI 53640	[1327-81-7]	
1926	chlorine fast black dye from *p*-(2-naphthylamino)phenol	Indocarbon CL	Sulfur Black 11	CI 53290	[1327-14-6]	10
1932–1934	clear violet-to-blue dyes from sub-stituted trichlorophenoxazones	Immedial New Blue 5RCF	Sulfur Blue 12	CI 53800	[1327-96-4]	11
		Immedial Bordeaux 3BL	Sulfur Red 7	CI 53810	[1327-97-5]	
1935–1938	fast browns from decacyclene (**8**) and its polynitro derivatives, using S_2Cl_2 as sulfurization agent or baking with sulfur	Immedial Katechu 4RL	Sulfur Brown 52	CI 53320	[1327-18-0]	12
		Immedial Yellow Brown GL	Sulfur Brown 60	CI 53325	[1327-20-4]	
		Immedial Brown GGL	Sulfur Brown 51	CI 53327	[1327-22-6]	
	ready-to-dye liquid dyes from commer-cial powders/press cake by solution in sodium sulfide–sodium sulfhydrate mixture	Sodyesul Black 4GCF	Leuco Sulfur Black 1	CI 53185	[66241-11-0]	13
1940–1941	synthetic methods introduced for conversion of organic pigment-type dyes to sulfide soluble dyes	Thionol Ultra Green B	Sulfur Green 14Leuco Sulfur Red 14		[12227-06-4]	(14, 15)
1945	sulfurization with aluminum chloride–sulfur monochloride com-plex of organic dyes and pigments					16

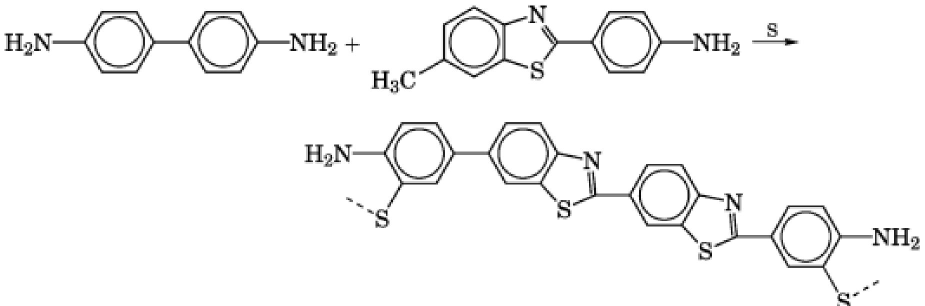
Table 1. ***Continued***

Year	Development	Product	CI designation Name	CI designation Number	CAS Registry Number	Ref.
1948	water-soluble dyes by conversion of conventional sulfur dyes with alkali sulfites/bisulfites to thiosulfonic acid derivatives	Thionol Black BM	Solubilized S Black 1	CI 53186	[1326-83-6]	
1959	condensation of intermediates con-taining NH_2 groups with cyanuric chloride; further conversion to thiol groups					17
1960	Inthion and Dykolite synthetic dyes; Bunte salts (alkyl- and arylthio-sulfato dyes) of nonsulfurized type	Inthion Brilliant Blue I3G	Condense S Blue 2	CI 18790	[12224-49-6]	
1966		Dykolite Brilliant Orange 3G	Condense S Orange 2			
1975	fast brown dyes from Indanthrene-type vat dyes by sulfurization with sulfur in chlorosulfonic acid					18

1.1.1. Sulfur Bake

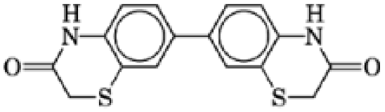
The yellow, orange, and brown sulfur dyes belong to this group. The dyes are usually made from aromatic amines, diamines, and their acyl and nuclear alkyl derivatives. These may be used in admixture with nitroanilines and nitrophenols or aminophenols to give the desired shade. The color formed is said to be the result of the formation of the thiazole chromophore, evident in dye structure (**1**).

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 (**1**).



(**1**)

The dye has been degraded by a fusion with caustic potash and the degradation products identified as various *o*-anilinyl mercaptans. They were identified and characterized by condensation with monochloroacetic acid to give the thioglycolic acids which, on acidification, were converted to well-defined crystalline lactams (**2–4**) together with a small amount of *p*-aminobenzoic acid.



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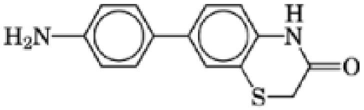

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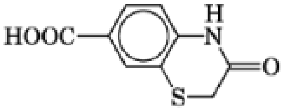
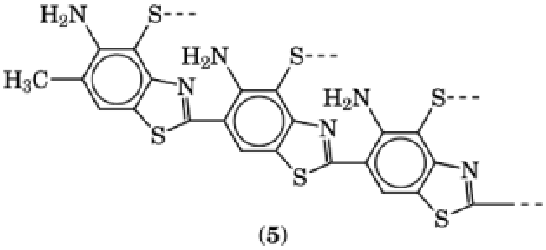


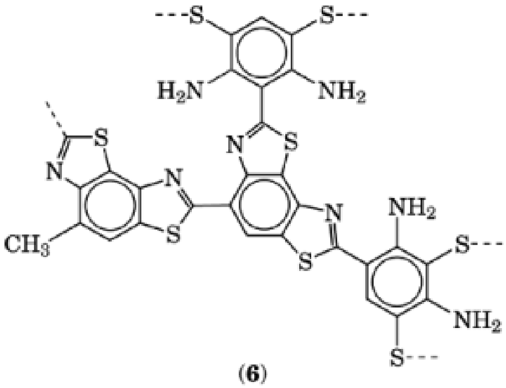
(4)

Investigation of Immedial Orange C, CI Sulfur Orange 1 [1326-49-4] (CI 53050), produced from 2,4-diaminotoluene (MTD) revealed ca 6–8 mols of MTD linked by thiazole rings. Whether the linkage is linear (**5**) or branched (**6**) was not ascertained with certainty but again showed that the thiazole chromophore is present.



(5)

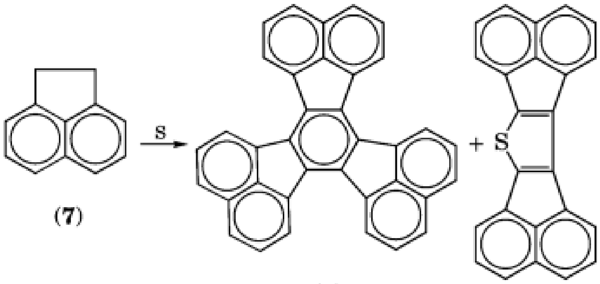
The solubility in alkali sulfide solutions stems from the presence of disulfide groups –S–S– in ortho position to the terminal amino groups. These disulfide groups are reduced to the mercapto groups –SH, which are soluble in alkali.



(6)

1.1.2. Polysulfide Bake

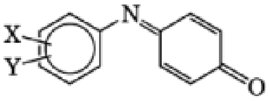
Although most dyes made formerly by this method are made by a polysulfide melt, some dyes where certain nitro and phenolic bodies prevent color formation in the sulfur bake are still made by this method. Prereduction of nitro groups substantially reduces the explosion hazard associated with heating these compounds with sulfur alone. Included in this class are also the exceptionally lightfast sulfur dyes derived from the polynitrodecacyclenes. Decacyclene (**8**) itself is made by a sulfur bake of acenaphthene (**7**) (20). Decacyclene is sulfur-baked to give CI Sulfur Brown 52. However, this color cannot be obtained from acenaphthene in a one-step sulfur bake because a significant amount of diacenaphtho[1,2-*b*;1′,2″-*d*]thiophene (**9**) is formed which, on sulfur baking, gives a dark brown dye of inferior lightfastness. The structure of the sulfur dyes derived from these polynuclear compounds is unknown.



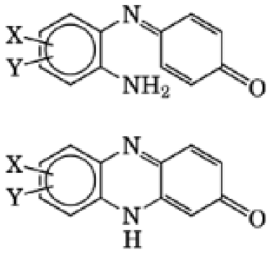
(**7**) (**8**) (**9**)

1.1.3. Polysulfide Melt

CI Sulfur Black 1 [1326-82-5] (CI 53185), derived from 2,4-dinitrophenol, is the most important dye in this group which also includes the indophenol-type intermediates. The latter are applied in the stable leuco form. The derived dyes are usually confined to violet, blue, and green shades. Other members of this group are intermediates capable of forming quinoneimine (**10**) or phenazone structures (**11**) that produce red-brown or Bordeaux shades:

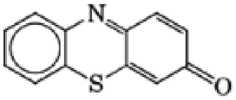


(**10**)



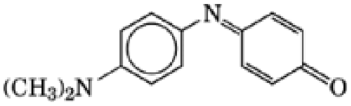
(**11**)

With the exception of the phenazones, these compounds lead to formation of the thiazinone ring structure (**12**) which closely resembles the phenazone ring system.

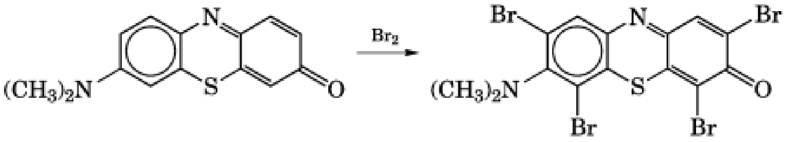


(**12**)

The structure of indophenol-type sulfur dyes was studied (21) on CI Sulfur Blue 9 made from the indophenol (**13**). This compound was purified and brominated to a tetrabromo derivative (**14**) identical with that obtained on bromination of Methylene Violet [2516-05-4] (**15**).

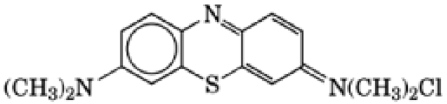


(**13**)



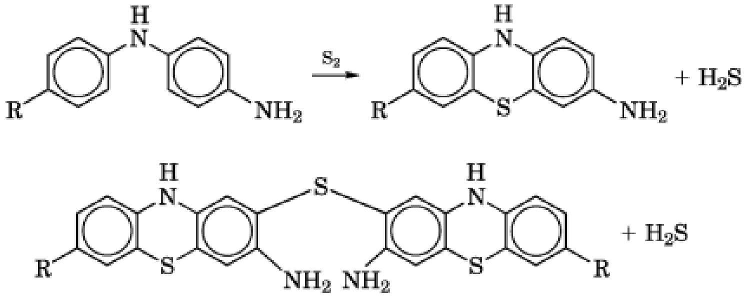
(**15**) (**14**)

Thus, the presence of a thiazine ring in CI Sulfur Blue 9 was conclusively proved. The thiazine ring is the fundamental chromophore that accounts for the high color value of both the sulfur dye and Methylene Blue [61-73-4], including their ability to form pale yellow leuco forms on reduction. Methylene Violet (**15**) is obtained from Methylene Blue (**16**) by hydrolysis in boiling alkali.



(**16**)

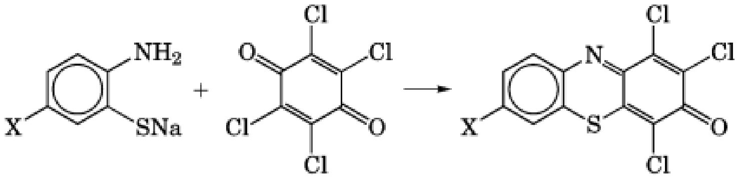
This work supports the suggestion that sulfur dyes are complex thiazines derived generally from diphenylamine units (22). Depending on the conditions of the thionation, two or more thiazine units could be linked by sulfur to produce a typical sulfur blue (**17**, R = OH or NH_2).



(17)

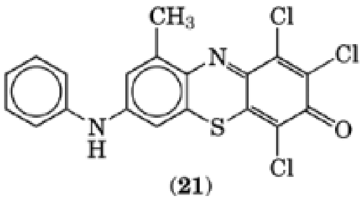
On more severe thionation, a third thiazine ring is formed to give a sulfur black. However, if hydroxyl groups instead of amino groups are attached at positions 2 and 2′, no ring closure would take place and the blue dye would be stable to heat. These formulas are general expressions for the nuclear structures of the blue-to-black sulfur dyes; they do not take into consideration the quinonoid formation of each dye and other aspects.

Further work elucidated the structure of the dyes in this group by synthesizing trichloroarylthiazinones (**18**) from an *o*-aminoaryl mercaptan (**19**) and chloranil (**20**); treatment with sodium disulfide replaced the halogens by mercapto groups.

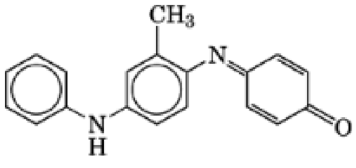


(19) **(20)** **(18)**

By this method, sulfur dyes derived from 4-hydroxydiphenylamine are seen to be essentially identical. Similarly, the sulfur dye from 7-anilino-9-methyl-1,2,4-trichlorophenothiazin-3-one (**21**) and the sulfur dye from 4-anilino-4′-hydroxy-2-methyldiphenylamine (**22**) were compared and found to be almost identical, as was the related trichlorophenothiazinone derivative (**23**) from carbazole when compared with Hydron Blue indophenol, CI Vat Blue 43 (CI 53630) (**24**).



(21)



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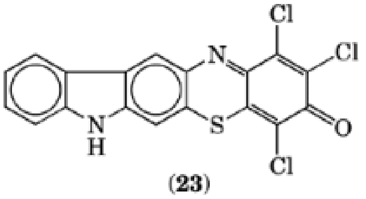

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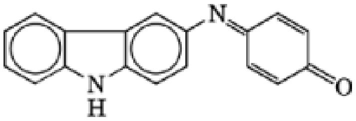


(24)

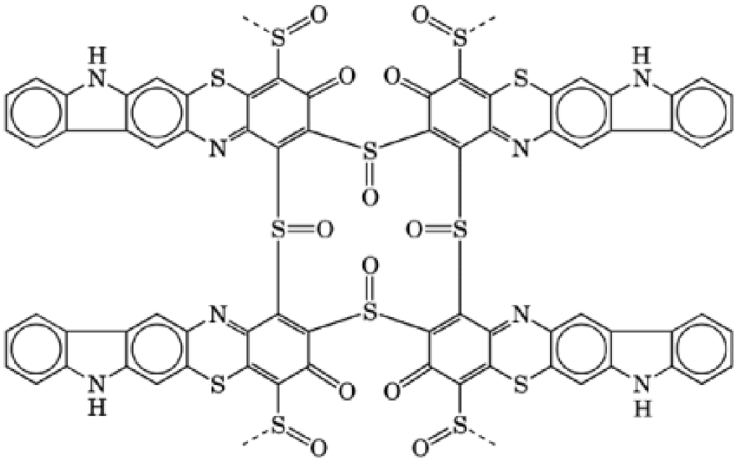
These formulas do not account for all the sulfur or oxygen found in the elemental analysis of the above dyes and formulas have been suggested whereby loosely bound sulfur is depicted as thiozonide or polysulfide sulfur. Oxygen is contained in sulfoxide groups (Fig. 1). For example, formula (**25**) has been suggested for CI Vat Blue 43 (23), formula (**26**) for a green dye from 4-amino-4′-hydroxydiphenylamine (24) and formula (**27**) for CI Sulfur Black 11 from 4-hydroxyphenyl-2-naphthylamine (25) (see Fig. 1). Although the structure of CI Sulfur Black 1, the most important of the sulfur dyes, has been investigated, it has not been established. Starting with 2,4-dinitrophenol, it was found that in color formation one mol ammonia is split off from 3 mol dinitrophenol, indicating that the structure consists of three benzene rings, an important factor that appears to be overlooked in the structural formulas published (26–29).

1.1.4. Sulfurized Vat Dyes

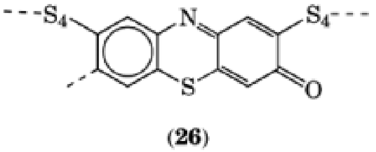
These dyes occupy an intermediate position between the true vat colors and sulfur dyes because, like vat dyes, they are dyed preferentially from a sodium dithionite–caustic soda bath. However, some dyes of this class can also be dyed from an alkali sulfide bath or a combination of the two, depending on the dyeing method used and the nature of the substrate to be dyed. This has led to some confusion because CI Vat Blue 42 and 43 are listed in the constitution section of the *Colour Index* under sulfur dyes. Although inferior to true vat dyes in fastness properties, they offer the advantage of better fastness, especially to chlorine, than conventional sulfur dyes.

In dyehouses where sulfide effluent is a problem, sulfur dyes of good chlorine fastness that dye satisfactorily from a dithionite–caustic alkali bath offer an advantage. Included in this group are CI Sulfur Black 11, CI Sulfur Red 10 [1326-96-1] (CI 53228), CI Sulfur Brown 96 [1326-96-1] (CI 53228), CI Vat Blue 42, and CI Vat Blue 43. The shades of these dyes can be brightened by the addition of vat dyes thus increasing the fastness of the resulting dye.

The structure of the sulfurized vat dyes is uncertain but in the presence of amino or methyl groups, thiazole-ring formation is possible. Examples have been confined to the dyes whose intermediates have been subjected to the conventional sulfur or polysulfide bake (Tables 2, 3, 4, 5).



(25)



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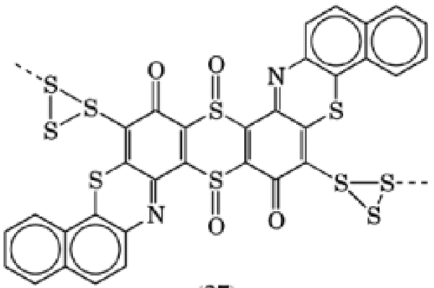


(27)

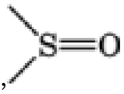
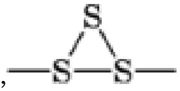
Fig. 1. Sulfur dyes incorporating sulfoxide,  (**25**), polysulfur (**26**), and thiozonoide,  (**27**) structures.

Table 2. Sulfur-Bake Dyes

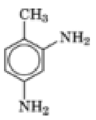
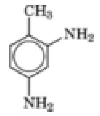
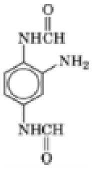
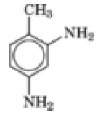
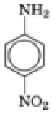
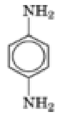
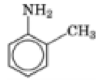
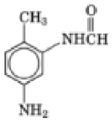
Intermediates	Shade	CI designation		CAS Registry Number
		Name	Number	
	orange	Sulfur Orange 1	CI 53050	[1326-49-4]

Table 2. ***Continued***

Intermediates	Shade	CI designation		CAS Registry Number
		Name	Number	
 	yellowish brown	Sulfur Brown 26	CI 53090	[1326-60-9]
 	yellowish brown	Sulfur Brown 12	CI 53065	[1327-86-2]
 	olive	Sulfur Green 12	CI 53045	[1236-48-3]
 	reddish yellowbrown	Sulfur Yellow 1Sulfur Brown 52	CI 53040CI 53320	[1326-47-2][1327-18-0]

2. Manufacture

2.1. Sulfur Bake

Thionation of the various aromatic amino or nitro compounds with sulfur was formerly carried out in iron pans 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. The spent H_2S is converted to Na_2S 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. The 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.

Table 3. Polysulfide-Bake Dyes

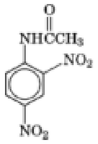
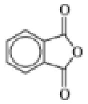
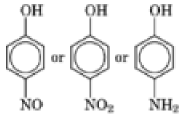
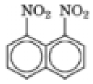
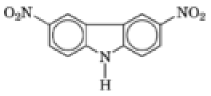
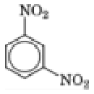
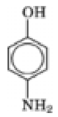
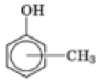
		CI designation		
Intermediate(s)	Shade	Name	Number	CAS Registry Number
 	yellow	Sulfur Yellow 9	CI 53010	[1326-40-5]
	dull reddish brown	Sulfur Brown 56	CI 53722	[1327-87-3]
	olivedull green	Sulfur Green 11Sulfur Green 1	CI 53165CI 53166	[12262-52-1][1326-77-8]
	brown	Sulfur Brown 31	CI 53280	[1327-11-3]

Table 3. ***Continued***

Intermediate(s)	Shade	CI designation		CAS Registry Number
		Name	Number	
	dull reddish brown	Sulfur Brown 7	CI 53275	[1327-10-2]
	brown	Sulfur Brown 6	CI 53335	[1327-25-9]
 	dull green	Sulfur Green 9	CI 53005	[1326-39-2]
	brownish olive	Sulfur Brown 4	CI 53210	[1326-90-5]

2.2. Fluid Polysulfide Melt

Thionation of the various indophenols is carried out in covered, jacketed, stainless-steel kettles fitted with agitator, thermometer, reflux condenser, and facilities for removal and absorption of the hydrogen sulfide gas liberated during thionation. When flammable solvents are employed in the melt, flameproof equipment is used. For bright shades, pure intermediates are used and iron is excluded. The sodium polysulfide may be screened to remove its main impurity, ferrous sulfide, which interferes when copper salts are added to the melt and may also have a dulling effect on the final shade. Shades are brightened by water-miscible solvents such as ethanol, butanol, glycerol, ethylene glycol, and Cellosolve. In some cases, the thionation is carried out entirely in solvent after first distilling off any water contained in the raw materials. In order to keep the melt fluid, hydrotropic substances such as urea, thiourea, or xylene sulfonates are added. Hydrotropic substances shorten thionation time and increase yield and brightness.

Metallic additions to the melt, usually in the form of copper sulfate, brighten the shade of certain dyes, such as the Bordeaux range made from phenazones and the greens made from the indophenols; the metal forms a complex with the dye. However, copper-containing dyes cannot be applied to material that requires vulcanization.

The composition of the polysulfide varies. It is generally applied in excess with the result that the final dye is wholly or partly in solution in leuco form. At this stage, it can be converted to a liquid form by suitable dilution and the addition of sodium hydrosulfide or diluted, if necessary filtered, and then precipitated by blowing air through the liquor or adding dilute acid. When stronger dyes are required, precipitation may be carried out by adding sodium nitrite directly to the final melt. The excess polysulfide is oxidized and ammonia liberated. Air blowing is usually continued in order to obtain the required brightness of shade. In some cases, caustic soda is added to partly dissolve the dye and air blowing is continued until a satisfactory shade is obtained. The dyestuff is then isolated by filtration, washed, air blown dry, discharged, and dried in a heated air oven.

Table 4. Polysulfide-Melt Dyes

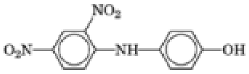
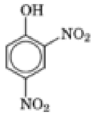
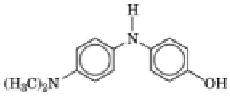
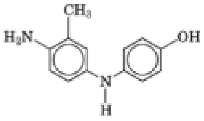
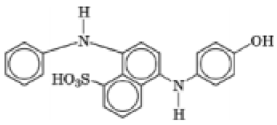
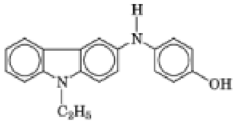
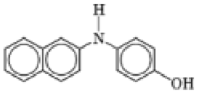
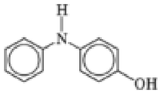
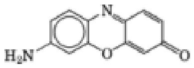
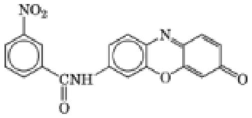
Intermediates	Shade	CI designation		CAS Registry Number
		Name	Number	
	bluish black	Sulfur Black 9	CI 53230	[1327-56-6]
	greenish black	Sulfur Black 1	CI 53185	[1326-82-5]
	bright blue	Sulfur Blue 9	CI 53430	[1326-97-2]
	reddish blue–bluish violet	Sulfur Blue 7	CI 53440	[1327-57-7]
	greenbluish green	Sulfur Green 3Sulfur Green 2	CI 53570CI 53571	[1327-73-7][1327-74-0]
	dull Bordeaux	Sulfur Red 3	CI 53710	[1327-84-0]

Table 4. ***Continued***

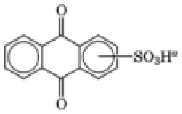
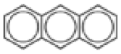
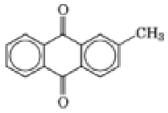
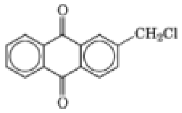
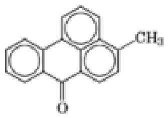
		CI designation		
Intermediates	Shade	Name	Number	CAS Registry Number
	Bordeaux	Sulfur Red 6	CI 53720	[1327-85-1]
	blue–reddish navy	Vat Blue 42	CI 53640	[1327-81-7]
	bluish black	Sulfur Black 11	CI 53290	[1327-14-6]
	Bordeauxbrown	Sulfur Red 10Leuco Sulfur Brown 96	CI 53228	[1326-96-1]
	reddish blue	Sulfur Blue 12	CI 53800	[1327-96-4]
	dull bluish red	Sulfur Red 7	CI 53810	[1327-97-5]

3. 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 quinonimine groups, further reduction takes place in a manner similar to the reduction of the keto group in vat dyes.

In the 1995 edition of the *Colour Index*, 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) (30).

Table 5. Sulfurized Vat Dyes

Intermediate	Shade	CI designation		CAS Registry Number
		Name	Number	
 [a]	yellowish brown	Vat dye	CI 58820	[1328-11-6]
	olive	Vat Green 7	CI 58825	[1328-12-7]
	yellowish orange	Vat Orange 21	CI 69700	[1328-39-8]
	yellow	Vat Yellow 21	CI 69705	[1328-40-1]
	dull greenish bluegreen	Vat Blue 7Vat dye	CI 70305CI 70310	[6505-58-4]

[a] Mono or di.

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 (see Dyes, environmental chemistry). 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.

Sodium polysulfide solutions (2–5 g/L), as antioxidants, prevent bronzing. Glucose has been used for a similar purpose and sodium borohydride effectively prevents bronzing when dyeing sulfur black. Other dyebath

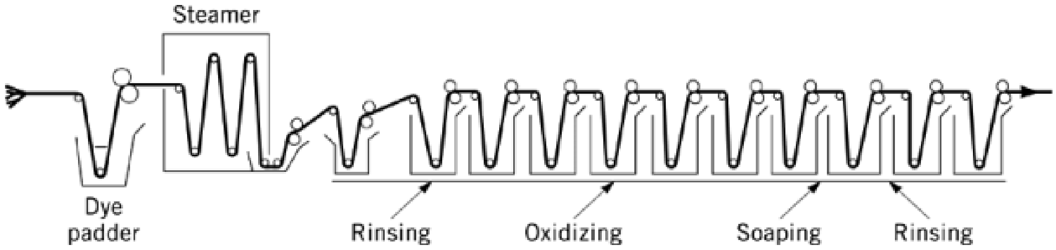


Fig. 2. Continuous operation of pad–steam dyeing.

additives, such as wetting and antifoam agents, may not be compatible with the reducing agents, so must be carefully selected.

The conventional sulfur dye powder is made into a paste with a small amount of soft water and an alkali-stable wetting agent. Boiling for a few minutes in a strong solution of sodium sulfide reduces the dye. The dissolved dye is diluted to the required dyebath volume. When dyeing pale shades, the final bath should contain at least 5 g/L sodium sulfide (60%), irrespective of the amount used to dissolve the dye.

The leuco sulfur dyes are in a prereduced form. They are produced in liquid form by dissolving paste from the parent sulfur dye in a reducing agent containing sodium sulfhydrate and alkali and, occasionally, other hydrotropic agents. These products were first introduced into the United States in 1936 and are available mainly from five manufacturers. They are true solutions requiring only to be diluted with water. Small amounts of reducing agents should be added depending on the dyeing method and the depth of shade required. Solubilized sulfur dyes have no real affinity for the fiber until they are converted into their leuco compounds by a reducing agent. After exhaustion on the fiber, rinsing and oxidation is effected in the same way as for the other types. Solubilized sulfur dyes can be used in aqueous solution to prepad the fabric which can then be treated with reducing agent, with intermediate drying in order to give more level dyeings. Cross-wound packages of yarn may be dyed by this two-stage method. The dyes may be applied in the conventional way by using a leuco dyebath from the start, but it is recommended that they be first dissolved in water only and that the reducing agent is added to the dyebath separately before dyeing.

In the pad–steam method, the padding liquor is prepared by adding the required quantity of prereduced liquid sulfur dye to water at 25–40°C together with additional chemicals and auxiliaries, depending on the dye and depth of shade desired. The padding liquor is fed into the trough of the dye padder which is fitted with a constant leveling device and temperature control. A padding mangle squeezes the well-prepared fabric evenly to provide a pickup of 50–80% of its own weight. The steamer, which should be free from air when operating, is generally set at 102–104°C. A dwell time of 60 s is usually adequate. The remainder of the equipment consists of washing and aftertreatment boxes through which the fabric passes successively before being dried. The continuous operation used in this process is depicted in Figure 2. A typical padding liquor recipe for a sulfur navy blue shade on 100% cotton drill is given in Table 6.

Blends of polyester with cotton (qv) 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 (31). The dye, together with urea and thiourea or similar compounds, is padded on 100% cotton, then dried and thermofixed at 150–175°C. 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 (32). Other uses of finely dispersed sulfur dyes without reducing agents have been described (33).

Table 6. Padding Liquor Recipe at 30°C

Ingredient	g/L[a]
Sulphol Liquid Dark Blue QL (JR)	150
Leucad 71 sodium sulfhydrate, 35%	5
caustic soda 100%	0.5
anionic wetting agent	2.0[b]
EDTA[c]-based sequestrant	0.5

[a] Unless otherwise stated.
[b] mL/L.
[c] EDTA = ethylenediaminetetraacetic acid.

Before the pressurized package dyeing machine became established, sulfur dyes were often employed for dyeing cotton warps in rope form (ball warps). The yarn in ropes or cables, which had been doubled into a W-form, was passed several times through a series of baths of reduced dye liquor and baths of rinsing water with intermediate squeezing. The depth of shade was gradually built up; the method resulted in a dyeing of excellent uniformity of shade across a woven fabric. This method is rarely used in the 1990s.

A variation is applied where warps for denims are first dyed with sulfur black or blue and then with indigo. The sulfur dye in its reduced form is added to the prewetting or scouring bath. The yarn is passed through and rinsed before passing to the part of the machine where the indigo is applied by the traditional method of successive stages of impregnation and air oxidation. The sulfur dye improves the appearance and reduces the quantity of indigo required.

3.1. Aftertreatment

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. However, because of ecological restrictions on bichromates, other oxidizing agents are coming into use, such as hydrogen peroxide, sodium perborate, 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.

3.2. Tendering Effects

Cellulosic materials dyed with sulfur black have been known to suffer degradation by acid tendering when stored under moist warm conditions. This effect may result from the liberation of small quantities of sulfuric acid which occurs when some of the polysulfide links of the sulfur dye are ruptured. A buffer, such as sodium acetate, or a dilute alkali in the final rinse, especially after oxidation in acidic conditions, may prevent this occurrence. Copper salts should never be used with sulfur black dyes because they catalyze sulfuric acid generation. Few instances of tendering with sulfur dyes other than black occur and the problem is largely confined to cotton.

Table 7. Principal Sulfur Dye Manufacturers and Products

Range name	CI classification	Manufacturer	Country
Asathio	sulfur	Asahi Chemical Co.	Japan
Cassulfon	leuco sulfur, liquid	Dystar	Germany
Diresul	leuco sulfur, liquid	Clariant Corp.	Spain
Endurol	vat, sulfurized vat dyes	James Robinson, Ltd.	United Kingdom
Episol	solubilized sulfur[a]	James Robinson, Ltd.	United Kingdom
Hydron	vat, sulfurized vat dyes	Dystar	Germany
Hydrosol	solubilized sulfur	Dystar	Germany
Immedial	sulfur	Dystar	Germany
Indocarbon	sulfur, dispersed form	Dystar	Germany
Kayasol	solubilized sulfur	Nippon Kayaku Co., Ltd.	Japan
Kayaku Homodye	sulfur, dispersed form	Nippon Kayaku Co., Ltd.	Japan
Pirocard	sulfur	Clariant Corp.	Spain
Pirosol	solubilized sulfur	Clariant Corp.	Spain
Sodyeco Liquid	sulfur, sulfurized vat dyes, liquid	Clariant Corp.	United States
Sodyesul	leuco sulfur	Clariant Corp.	United States
Sodyevat	vat, sulfurized vat dyes, dispersed form	Clariant Corp.	United States
Sulphol	sulfur	James Robinson, Ltd.	United Kingdom
Sulphol Liquid	leuco sulfur, liquid	James Robinson, Ltd.	United Kingdom
Sulphosol	solubilized sulfur	James Robinson, Ltd.	United Kingdom
Youhaodron	vat, sulfurized vat	China National Chemi-cals Import and Export Corp.	People's Republic of China
Youhao Sulphur	sulfur		

[a] For leather.

4. Economic Aspects

The low cost of sulfur dyes, coupled with good fastness properties and the ease of application, continues to ensure a high consumption. The number of manufacturers has fallen since the 1960s and production is mainly confined to the United States, U.K., Germany, and Spain. There is one principal producer in each of these countries. There are other, less well-known manufacturers in Russia, the People's Republic of China, South Korea, Japan, and Brazil (Table 7).

Few production figures have been available since 1966, when sulfur dyes represented 9.1% of total U.S. dye production and 15.8% of the dyes made for use on cellulosic fibers. World production is estimated at 110,000–120,000 t/yr. This is the highest percentage of any group of dyes. In terms of value, however, the picture is very different because the dyes are relatively inexpensive.

5. Commercial Forms of Sulfur Dyes

5.1. Powders

Powders have, in the past, been the principal form in which sulfur dyes were sold. In general, they are made from the dried press cake, finely ground, and standardized with common salt, sodium sulfate, or soda ash. They are prepared for dyeing by making a paste with water, which is dissolved by boiling with the necessary amount of reducing agent and further addition of water.

5.2. Prereduced Powders

These are usually made from press cake paste to which a reducing agent has been added, such as sodium sulfide, sodium hydrosulfide, or sodium dithionite, which solubilize the dye in water. Before drying, the dye paste may be mixed with dispersing and stabilizing agents to aid application.

5.3. Grains

Grains are usually prereduced powders. The quantities of sodium sulfide, hydrosulfide, and mineral salts are adjusted to give a grainy product when the paste slurry is dried on a steam-heated drum dryer. Grains offer the advantage of not being dusty.

5.4. Dispersed Powders

The principal use of dispersed powders is in pad–dry–chemical pad–steam dyeing techniques. They are normally made from press cake by ball or bead milling to microparticle size in the presence of dispersing agents. The drying is strictly controlled and is carried out in the presence of anticoagulants to prevent aggregation of the dispersed dye particles.

5.5. Dispersed Pastes

The milled pastes vary in strength, but for ease of handling the consistency of the dispersed pastes generally permits pouring from the container. Because there is no drying step, dispersed pastes are usually cheaper than dispersed powders.

5.6. Liquids

Some liquid dyes are made directly from the thionation melt by additions of caustic soda and sodium hydrosulfide. Hydrotropic substances are sometimes added, either at the initial thionation stage or after the polysulfide melt is finished in order to keep the reduced dye in solution. Partly reduced liquids are also available. They are usually more concentrated than fully reduced liquids, thus saving packaging and transportation costs. However, they require a further addition of reducing agent to the dyebath in order to obtain full color value. On the other hand, fully reduced liquids are ready to use, because the amount of reducing agent for each dye has been carefully controlled in order to obtain maximum stability on storage and maximum color yield in use. They are not affected by low temperatures as are the dispersed pastes.

5.7. Water-Soluble Brands

Water-soluble sulfur dyes occur in both powder and liquid form. The liquid product is cheaper because no drying step is required. These dyes are the Bunte salts, or thiosulfuric acid derivatives of the sulfur dyes. They are made by warming the polysulfide-free pastes with sodium sulfite or bisulfite until they are water soluble. They are salted out from solution or isolated by drum drying the liquor. Aqueous solutions of these dyes show little or no affinity for cellulosic fiber until a reducing agent has been added and, therefore, they penetrate tightly woven materials and give level dyeings with less tendency to bronzing.

6. Health and Safety

During the 1980s and 1990s, much more emphasis has been placed on health and safety aspects within the chemical and dyestuff industries. As a consequence, benzidine and β-naphthylamine, which are known carcinogens, have been banned in many countries. In some cases, alternatives to these intermediates have been found in order to retain dyestuffs with similar shades and properties. For example, bright yellow to orange sulfur dyes are obtained from a sulfur bake of 4-(6-methyl-2-benzothiazolyl)aniline, *N,N′*-diformyl-*p*-phenylenediamine, and 2,2′- or 4,4′-diformyldiaminodiphenyl disulfide (34). These shades were previously obtainable only from mixtures containing benzidine. The handling of hazardous chemicals such as nitroanilines, dinitro- and diaminotoluenes, nitro- and dinitrophenols, and chlorodinitrobenzenes is kept to a minimum. In all cases, suitable protective gear is employed. Hydrogen sulfide is one of the chief hazards of sulfur dye manufacture and is usually removed by caustic soda scrubber units. Accidental escape of H_2S can be detected by a system that incorporates detector heads specifically for hydrogen sulfide. Process sheets should list all the hazards associated with each operation.

The effluent from the dye manufacture and textile dyeing industry is usually treated by aeration in large tank farms. The aeration equipment may be a floating rotary blade beater or vertical helix columns through which compressed air is passed or alternatively dissipated through venturi pipes. By these means, ca 10–12% of the oxygen in the air can be effectively utilized in the degradation of the sulfur dye waste, rendering it acceptable to municipal sewage treatment farms. Small dye houses utilize spent flue gases or hydrogen peroxide as well as ferrous salts to treat plant effluent. However, such an operation is more costly and mixing with spent bleach liquors may reduce costs. Anthraquinone sulfonic acids can be used as catalysts to assist aeration.

7. Uses

The sulfur dyes are widely used in piece dyeing of traditionally woven cotton goods such as drill and corduroy fabrics (see Textiles). 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. 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 (35). 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.

Cotton yarn is dyed in package machines and the dye exhausted by increasing the temperature and adding salt. The dye must be completely dissolved when preparing the dyebaths to avoid contamination with undissolved dye in the yarn package. The increased availability of the prereduced liquid dyes and the improved quality of sodium sulfide have reduced this problem. Incorrectly dissolved dye was previously the cause of most faulty dyeings.

Continuous dyeing of piece goods by pad–steam methods is one of the principal outlets for sulfur dyes, mostly in prereduced liquid form. Nontextile uses for sulfur dyes are limited. Sulfur Black is used for dyeing paper, particularly for lamination applications. Leather dyeing is done with the solubilized sulfur Episol dyes. These dyes give well-penetrated dyeings with far better wetfastness than is usually obtained with acid or direct dyes. The dyes are applied to the neutralized leather at pH 7.5–8.0 without reducing agents, and are fixed in a manner similar to the fixation of acid dyes with formic acid at pH 3.8.

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