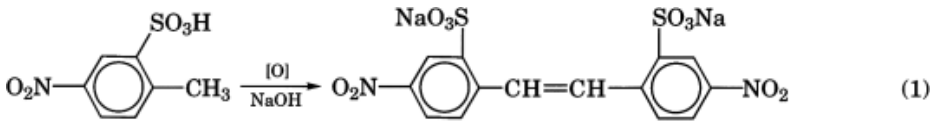
Kirk-Othmer Encyclopedia of Chemical Technology.

STILBENE DYES

Stilbene dyes of importance are mostly direct yellow dyes for cellulosic fibers, especially paper. There have been several red and blue stilbene-containing dyes reported, but they have not (ca 1996) been developed to commercial importance. There are brown leather dyes which are stilbene-based. The most important stilbene dyes are those known since the 1880s. The commercial importance of Direct Yellow 11 (1883), Direct Orange 15 (1888), Direct Yellow 4 (1886), and Direct Yellow 106 (1936) attest to the value, properties, and durability of stilbene yellow dyes.

Stilbene [103-30-0], $C_6H_5CH{=}CHC_6H_5$, is a crystalline hydrocarbon used in the manufacture of dyes; its name is derived from the Greek word *stilbein*, meaning to glitter (1). However, in all the references to commercial dyes, there is not a single one derived directly from stilbene itself nor is there a reference to anyone ever making a dye from stilbene. In most examples, the starting material for stilbene dyes is 4-nitrotoluene-2-sulfonic acid [121-03-9], which is oxidized under alkaline conditions to 4,4′-dinitro-2,2′-dinitrostilbenedisulfonic acid [128-42-7] **(1)** as the first descriptive substance. There are more than 100 stilbene dyes listed in the *Colour Index* which have been offered as commercial products (2); less than 12 are available, as listed in the latest *AATCC Buyer's Guide* (3).

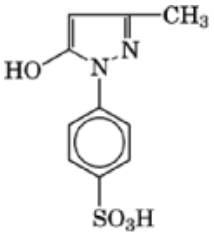
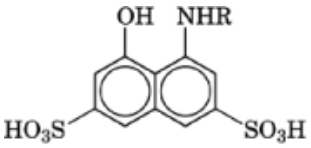
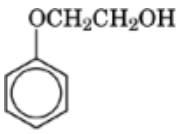
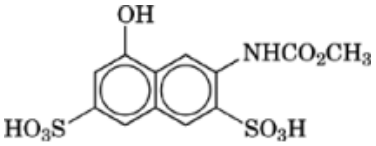
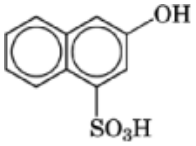


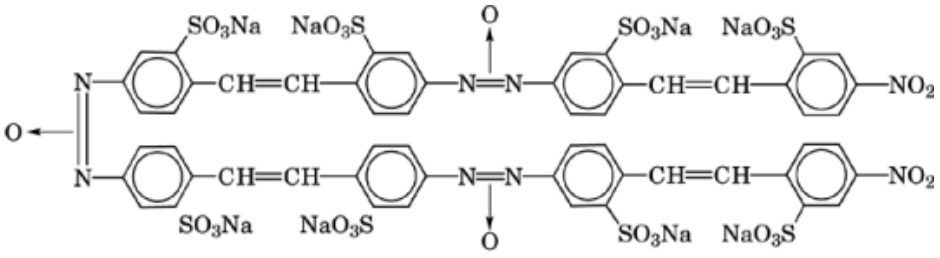
(1)

Stilbene dyes are classed as a subgroup of azo dyes having excellent colorfastness and typical direct dye wash fastness on cotton and are arranged into six categories by the Society of Dyers and Colourists (2), as described in the following.

(*1*) Self-condensation products of 4-nitrotoluene-2-sulfonic acid or its derivative 4,4′-dinitro-2,2′-stilbenedisulfonic acid or 4,4′-dinitro-2,2′-dibenzyldisulfonic acid [728-42-7] and products of their treatment with reducing or oxidizing agents. An example is Direct Yellow 11 (CI 40000) [1325-37-7] **(2)** .

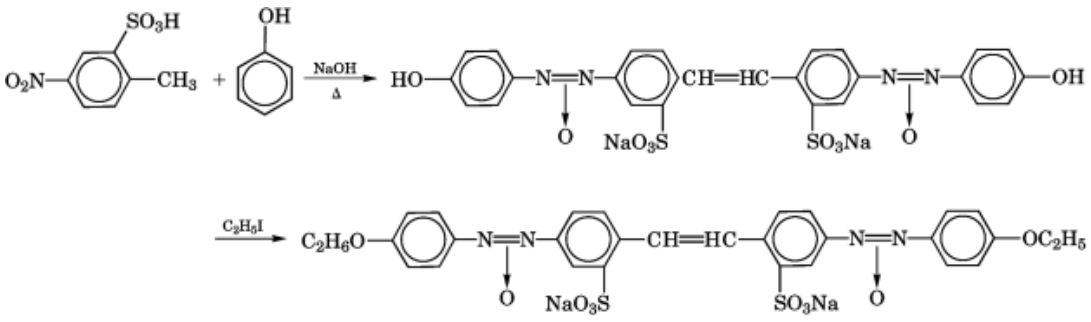
Table 1. Dyes Derived from Tetrazotized (7) Dye or Coupling Compound

Coupling component	CAS Registry Number	Ref.	Color
	[91779-63-4]	12	yellow
 R = CH_3CH_2— CH_2OHCH_2— $CH_3CH_2CHOHCH_2$—		15	blue
		16	yellow
o-cresol		18	yellow
	[118914-79-7]	11	brown
		11	brown



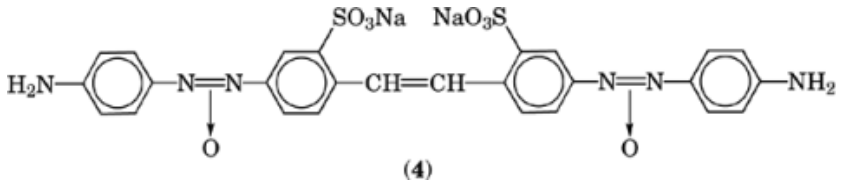
(**2**)

(*2*) Condensation products of 4-nitrotoluene-2-sulfonic acid or its derivatives together with phenols, naphthols, or aminophenols. An example here is Direct Yellow 19 (CI 40030) **(3)**:



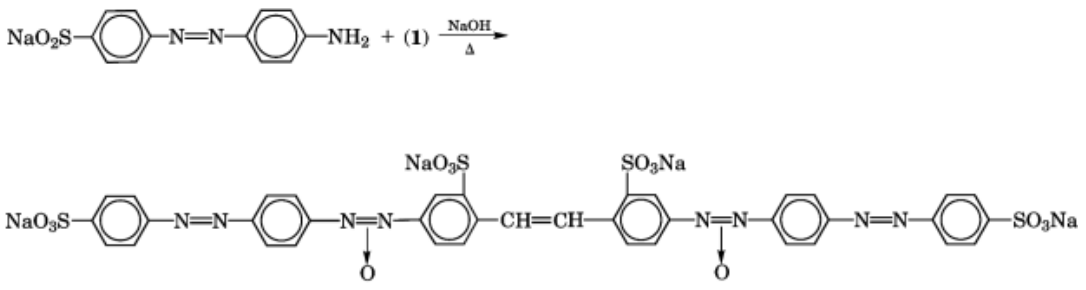
(3)

(*3*) Condensation products of 4-nitrotoluene-2-sulfonic acid or its derivatives together with aromatic amines. Direct Orange 28 (CI 40065) **(4)** is an example. The amine in this case is *para*-diaminobenzene.



(4)

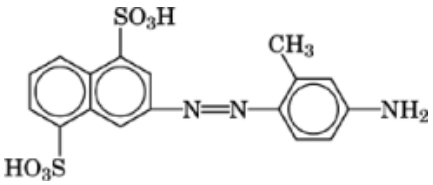
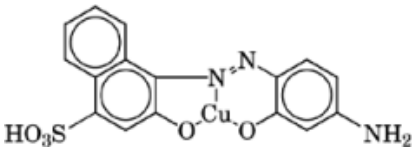
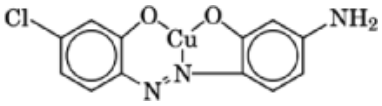
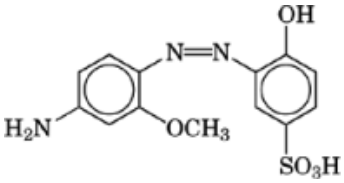
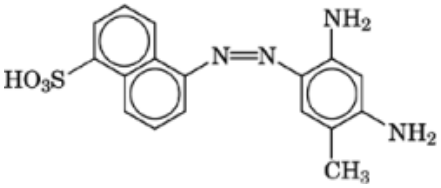
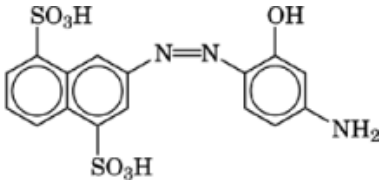
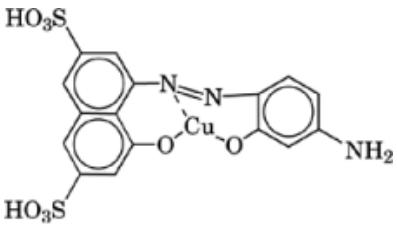
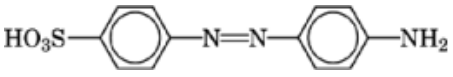
(*4*) Azo-stilbene dyes formed by condensation of 4,4′-dinitro-2,2′-stilbenedisulfonic acid or 4,4′-dinitro-2,2′-dibenzyldisulfonic acid **(1)** with aminoazo compounds. Direct Orange 34 (CI 40215) [32651-66-4] **(5)** is a representative:

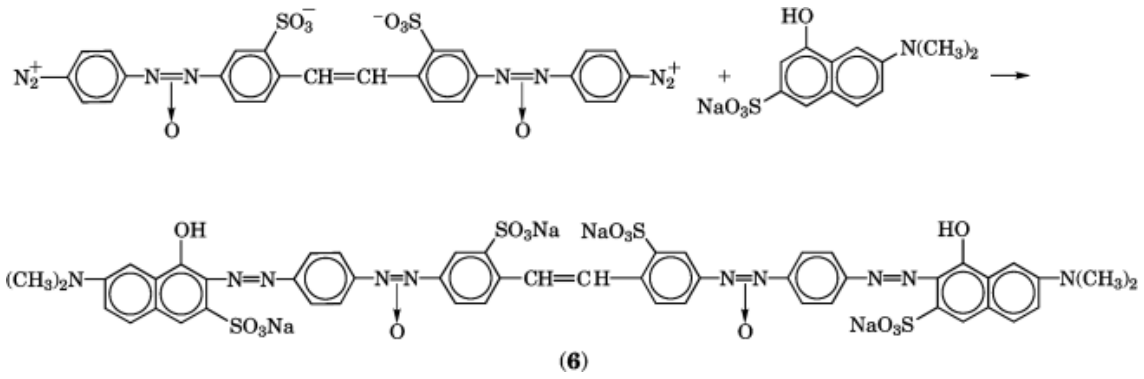


(5)

(*5*) Azo-stilbene dyes formed by diazotization of a condensation product containing primary amino groups and coupling with azo dye coupling components, eg, Direct Brown 29 (CI 40505) **(6)**:

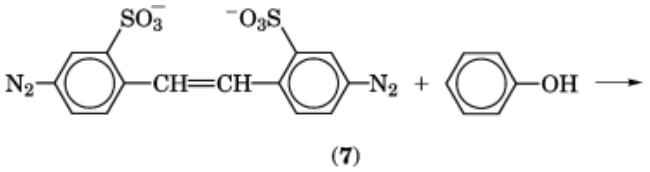
Table 2. Brown Dyes Derived From (1)

Coupling component	CAS Registry Number	Ref.
	[106199-75-1]	(19, 29)
	[106564-02-7]	21
	[106222-76-8]	23
	[85895-92-7]	24
	[84373-09-1]	25
	[106769-40-8]	(20, 26)
		27
	[102949-51-9]	30

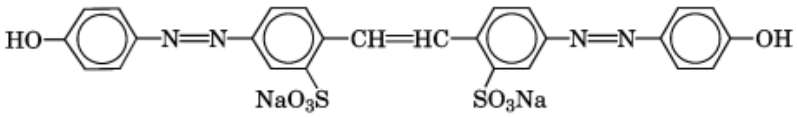


(**6**)

(*6*) Stilbene-azo dyes of more precise constitution prepared in the usual way by tetrazotization and coupling of 4,4′-diamino-2,2′-stilbenedisulfonic acid [81-11-8] **(7)**. The product in this example is ZDirect Yellow 4 (CI 24890) [3051-11-4] **(8)**:



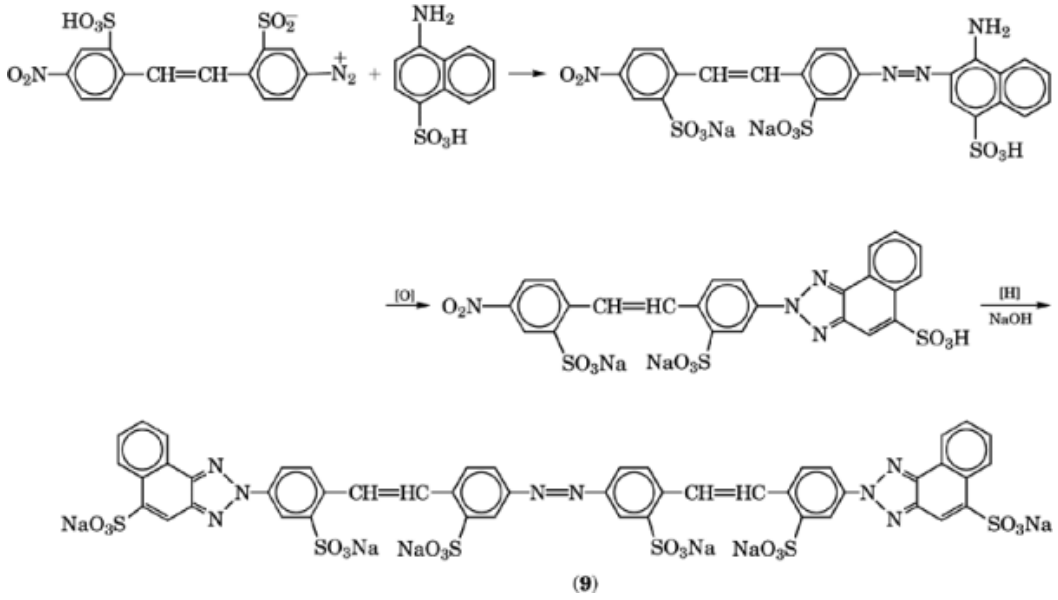
(**7**)



(**8**)

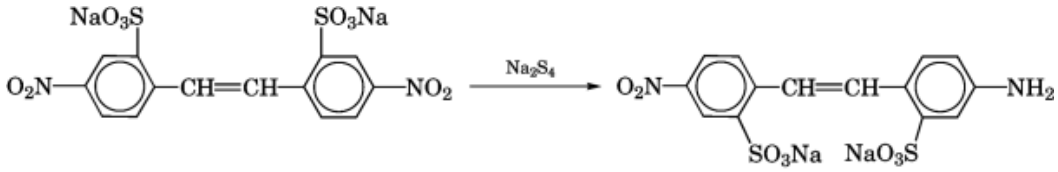
(*6a*) Stilbene-azo dyes from 4-nitro-4′-amino-2,2′-stilbenedisulfonic acid [119-72-2] include Direct Yellow 106 (CI 40300) [12222-60-5] (**9**). The synthetic route is shown in Figure 1.

Most stilbene dyes derived from 4-nitrotoluene-2-sulfonic acid are of nondefinitive structure even though structures are proposed which are descriptive of the major components (4). 4-Nitrotoluene-2-sulfonic acid can be converted to 4,4′-dinitro-2,2′-dinitrostilbenedisulfonic acid **(1)** in yields of 60–80% by heating in dilute sodium hydroxide (3%) at about 50°C and slowly adding sodium hypochlorite (4), as shown in equation **1**. The product obtained can be reduced to 4,4′-diamino-2,2′-stilbenedisulfonic acid **(7)**, then tetrazotized and coupled to various phenols and amines to give dyes having reasonably definitive structures. These dyes are classed as normal azo dyes (2). As may be expected with most tetrazotizations and couplings, many decomposition and self-coupled by-products are obtained. 4,4′-Dinitro-2,2′-stilbenedisulfonic acid **(1)** can also be reduced with polysulfide to 4-nitro-4′-amino-2,2′-stilbenedisulfonic acid **(10)**, which is a useful intermediate for dye synthesis.



(**9**)

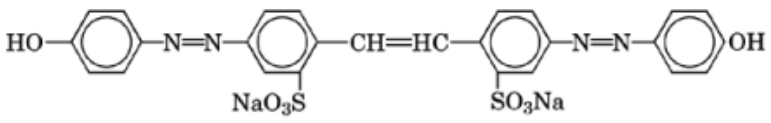
Fig. 1. After diazo coupling, oxidation leads triazene ring formation. Alkaline reduction and coupling lead to (**9**).



(**1**) (**10**)

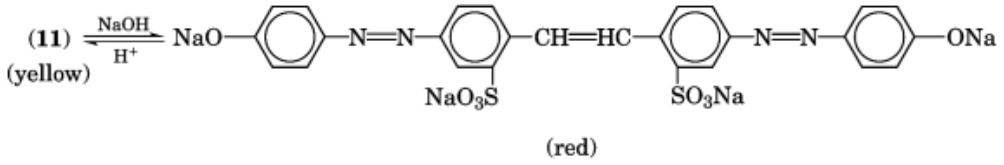
Stilbene dyes have generally been important as direct dyes and fluorescent brighteners for cellulosic fibers (4). Most stilbene dyes are yellow and orange, with some examples of reds and browns and even a few blues. Brown stilbene dyes have commercial value as leather dyes (4).

Direct Yellow 4 (CI 24890) **(11)** is the most familiar dye made from tetrazotized 4,4′-diamino-2,2′-stilbenedisulfonic acid [57153-16-9] **(7)** and phenol.



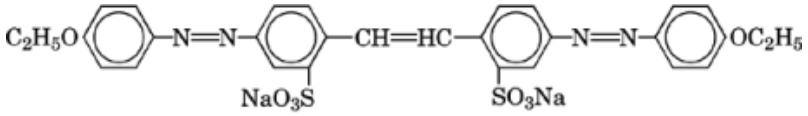
(**11**)

This dye has importance for dyeing paper and is also used as a pH indicator, changing to a red color under alkaline conditions.



(red)

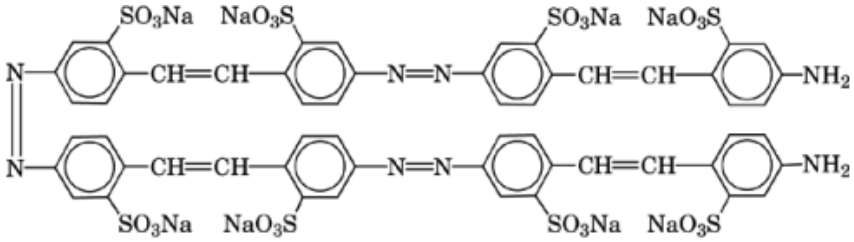
An alkali-stable dye, Direct Yellow 12 (CI 24895) [2870-32-8] **(12)**, is made by ethylating Direct Yellow 4 **(11)** with ethyl chloride or diethyl sulfate.



(12)

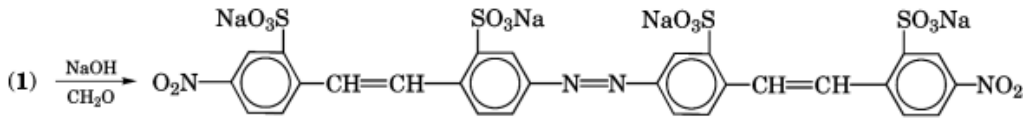
Condensation dyes from 4-nitrotoluene-2-sulfonic acid are the most important of the stilbene dyes. Direct Yellow 11 (CI 40000), discovered in 1883 and commonly known as Sun Yellow [1325-37-7], is widely used in the paper industry (2, 4).

Direct Orange 15 (CI 40003) [1325-35-5] **(13)**, which is made by reducing the alkaline condensation product equivalent to Direct Yellow 11 with sulfide or formaldehyde, is an important paper dye used in dyeing brown paper for bags.



(13)

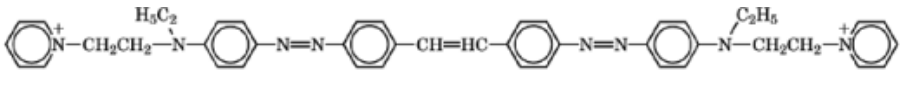
The azoxy and nitro groups in Direct Yellow 11 are reduced to azo and amino groups in Direct Orange 15. Direct Yellow 6 (CI 40006) **(14)** is a greener and brighter shade of yellow than Direct Yellow 11 and is made by reductive azo formation from 4,4′-dinitro-2,2′-stilbenedisulfonic acid to an azo and azoxy dye.



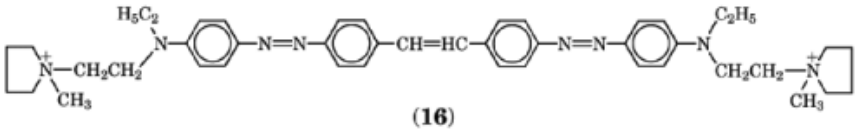
(14)

This controlled synthesis gives a purer product than alkaline condensation of 4-nitrotoluene-2-sulfonic acid alone and is the reason for its brightness (4).

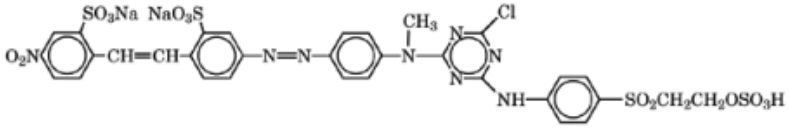
Activity in this class of compounds since the early 1980s has been mostly with stilbene fluorescent brighteners (see Fluorescent whitening agents). There has, however, been some other activity in most of the six listed categories of dyes as well. 4-Nitrotoluene-2-sulfonic acid condensations to give stable solutions of



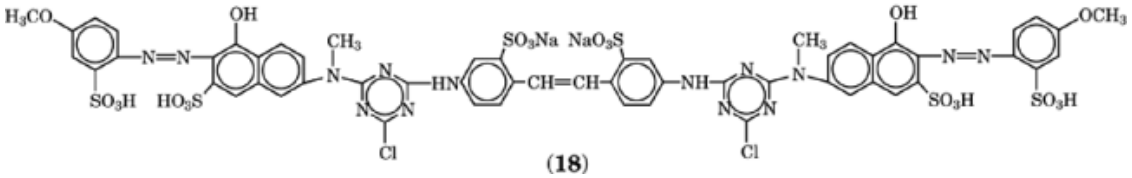
(**15**)



(**16**)



(**17**)



(**18**)

Fig. 2. Basic and reactive stilbene dyes: (**15**) [122749-45-5] (32); (**16**) [122749-47-7] (33); (**17**) [89049-99-0] (10); and (**18**) [79146-01-3] (13).

Direct Yellow 11 type dyes for paper account for many efforts in this category (5–9). Reaction products of 4,4′-diamino-2,2′-stilbenedisulfonic acid tetrazo with various coupling components are claimed as dyes for paper (10–18) (Table 1).

The most widely reported developments have been in category 4, ie, 4,4′-dinitro-2,2′-stilbenedisulfonic acid **(1)** condensations with amino-containing azo components, some of which are copper complexes, to give dyes having excellent properties on leather (19–31) (Table 2).

Tetrakisazo dyes with good fastness properties prepared by tetrazotization of **(7)** coupling to 1-naphthylamine, retetrazotizing and coupling to, eg, 2-naphthol, have been reported (14). Limited use is also reported for both basic and reactive stilbene-containing dyes (10, 13, 32, 33) (Fig. 2). Although it is reported that basic dyes are suitable for dyeing paper, none is found in commerce.

Coupling tetrazo **(7)** with *o*-cresol has been reported to give a dye **(19)** which is less alkali-sensitive than Direct Yellow 4 (CI 24890) and to have better cold-water solubility than Direct Yellow 12 (CI 24895) (18). One reference is made to a stilbene laser dye (10) and two each to dyes for light-polarizing films (34, 35) and reprographic inks (36, 37).

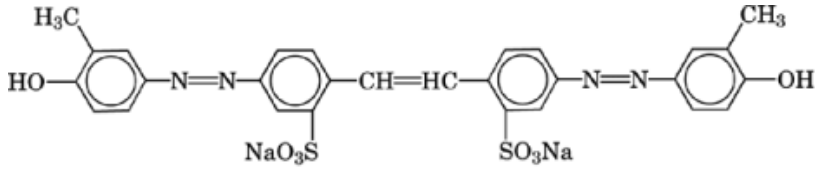
Table 3. Estimated Production Volume and Prices of Stilbene Dyes

	Volume, 10^3 kg		Average sales price, $/kg		
Dye	Liquid	Powder	Liquid	Powder	Manufacturer
Direct Yellow 4	455	23	2.20	6.60	BASF, DyStar, C & K
Direct Yellow 6	205	36	1.87	5.83	BASF, Ciba, C & K
Direct Yellow 11	2730	114	1.98	4.40	BASF, DyStar, Ciba, C & K
Direct Orange 15	136	23	2.75	7.15	DyStar, C & K
Direct Yellow 106		91		19.80	Ciba, C & K

Table 4. Toxicological Data for Stilbene Dyes

Dye	LD_{50}, mg/kg[a]	LC_{50}, mg/L	BOD, mg O_2/g	COD, mg O_2/g
Direct Yellow 6	>5000	>1000 (96 h) (fat head minnow)	13	318
Direct Yellow 11	>5000	>280 mg/m (4 h) inhalation (rat)	100	6600
Direct Yellow 106	>7500	>1000 (48 h) (trout)	107	460
Direct Orange 15	>5000	>1000 (96 h) (blue gill)	200	6900

[a]Rat.



(**19**)

1. Economic Aspects

Direct Yellow 4, Direct Yellow 11, Direct Yellow 106, and Direct Orange 15 are the most important stilbene dyes, accounting for most sales of this type. Estimated volumes and values for liquid and powder forms appear in Table 3 (38).

2. Health and Safety Factors

Stilbene dyes are similar to azo dyes in their resistance to biological degradation. Typically the BOD is only a small percentage of the COD. Available toxicological data indicate relatively little personal or environmental hazard (39–42) (Table 4).

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