# DYES, AZO

## 1. Introduction

The term azo dyes is applied to those synthetic organic colorants that are characterized by the presence of the chromophoric azo group (–NN–). This divalent group is attached to $sp^2$ hybridized carbon atoms: on one side, to an aromatic or heterocyclic nucleus; on the other, it may be linked to an unsaturated molecule of the carbocyclic, heterocyclic, or aliphatic type. No natural dyes contain this chromophore. Commercially, the azo dyes are the largest and most versatile class of organic dyestuffs. There are more than 10,000 *Colour Index* (CI) generic names assigned to commercial colorants, approximately 4500 are in use and over 50% of these belong to the azo class (1). Synthetic dyes are derived in whole or in part from cyclic intermediates. Approximately two-thirds of the dyes consumed in the United States are used by the textile industry to dye natural and synthetic fiber or fabrics, about one-sixth is used for coloring paper, and the rest is used chiefly in the production of organic pigments and in the the dyeing of leather and plastic. Dyes are sold as pastes, powders, and liquids; concentrations vary from 6 to 100%. The concentration, form, and purity of a dye is determined largely by the use for which it is intended.

**1.1. Classification and Designations.** The most authoritative compilation covering the constitution, properties, preparations, manufacturers, and other coloring data is the publication *Colour Index*, which is edited jointly by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colorists (AATCC). In the *Colour Index* a dual classification system is employed to group dyes according to area of usage and chemical constitution. Because of the ease of synthesis of azo, disazo, and polyazo dyes, and their wide range of applications, azo dyes comprise the largest chemical class in numbers, monetary value, and tonnage produced. There are more than 2200 chemical structures of azo dyes disclosed in the *Colour Index* (Vols. 4–8).

Nearly all dye manufacturers use letters and numerals in the names of their products to define the hue. Thus B is blue; G, yellow (gelb in German) or green; R, red; and Y, yellow. Numerals, ie, 2G (or GG), 3G, 4G, etc indicate, in this case, a successively yellower or greener shade. Occasionally, suffixed letters are used to feature other properties such as solubility, lightfastness, brightness, and use on synthetic fibers.

Chemically, the azo class is subdivided according to the number of azo groups present into mono-, dis-, tris-, tetrakis-, etc. Mono- and disazo dyes are essentially equal in importance, trisazo dyes are less important, and tetrakisazo dyes, except for a few, are much less important. For this reason, substances with more than three azo linkages are generally included under the heading of polyazo dyes. The *Colour Index* lists the azo dyes as follows:

| *Chemical Class* | *Colour Index Number Range* |
|---|---|
| monoazo | 11,000–19,999 |
| disazo | 20,000–29,999 |
| trisazo | 30,000–34,999 |
| polyazo | 35,000–36,999 |

## 2. The Chemistry of Synthesis

Peter Griess synthesized the first azo dye soon after his discovery of the diazotization reaction in 1858. The two reactions which form the basis for azo dye chemistry are diazotization (eq. 1) and coupling (eq. 2) (2).

$$\mathrm{ArNH_2 + 2\,HX + NaNO_2 \longrightarrow ArN_2^+X^- + NaX + 2\,H_2O} \qquad (1)$$

$$\text{where } \mathrm{X = Cl^-,\ Br^-,\ NO_3^-,\ HSO_4^-,\ BF_4^-}, \text{ etc.}$$

$$\mathrm{ArN_2^+X^- + RH \longrightarrow ArN{=\!=}N{-\!-}R + HX} \qquad (2)$$

where R represents an alkyl or aryl radical whose conjugate acid RH is capable of coupling.

**2.1. Diazotization.** Practically every aromatic primary amine is a potential diazo component. The value of an amine as a diazo component is determined chiefly by the properties of the dye prepared from it. Cost of amine, ease of diazotization, stability of the diazonium salt, and final cost of dye are factors that influence the selection of an amine. There are many methods (3) described for the synthesis of diazo compounds. A technically important one involves treating a primary arylamine with sodium nitrite in the presence of mineral acid at 0–5°C to form a diazonium salt as shown in equation 1. Since the mechanism of diazotization involves attack by the nitrosating species on the free amine and not the amine salt, it is often necessary to choose a higher acid strength in order to complete diazotization of weakly basic amines such as nitroanilines and trihalogenoanilines. The reaction medium should also provide stabilization of the diazonium salt by solvation effects. Negatively substituted and, therefore, very weakly basic amines, for example, 2,4-dinitro-6-halogenoaniline, 2,4-dinitroaniline [97-02-9] or 2,6-dihalogeno-4-nitroaniline, are dissolved in a concentrated acid (sulfuric, phosphoric, or glacial acetic acid) and diazotized with nitrosylsulfuric acid [7782-78-7] $HSO_4 \cdot NO$. These diazos are relatively more stable in solution. Suspensions of diazonium salts in higher concentrations are dangerous and can form explosive mixtures (4). Amines containing sulfonic acid groups (zwitterions) are difficult to dissolve in acid medium. Such amines, for example, sulfanilic acid [121-57-3], metanilic acid [121-47-1], naphthionic acid [84-86-6], or diaminostil-benedisulfonic acid [81-11-8], can preferably be diazotized by the so-called indirect method. In this case, the sodium salt of the acid may be treated with the required amount of nitrite in aqueous solution, and this solution may be run into ice-cooled hydrochloric acid solution. Sometimes diazotization of aminophenols (qv) and aminonaphthols is carried out in the presence of catalytic amounts of copper or zinc salts (5). This suppresses the oxidation of the hydroxy groups to the corresponding quinones by nitrous acid. The diazotization of *o*-aminophenols and naphthols is important in relation to the synthesis of *o,o*′-dihydroxyazo metal complex dyes.

Dyes with heterocyclic diazo components have received much attention because of their high tinctorial power and excellent brightness. A few technically important heterocyclic amines used in their preparation are shown in Figure 1. Heterocyclic azo dyes from some of these amines offer excellent fastness properties and are commercially competitive with more expensive anthraquinone dyes. During the 1980s, a large number of patents were issued for dyes based on 2-aminothiophenes (6). The diazotization of heterocyclic amines has been reviewed (7), but no systematic methods are available. Protonation at the hetero ring can reduce the nucleophilicity of the primary amino group leading to an equilibrium between the amine and the diazonium ion. This equilibrium favors the protonated amine when the concentration of acid is increased (8). 2-Aminothiazoles and 2-aminobenzothiazoles are readily diazotized to diazonium salts with sodium nitrite or nitrosylsulfuric acid in strong acid such as sulfuric acid, phosphoric acid, or nitric acid. In concentrated hydrochloric acid the diazonium salts react

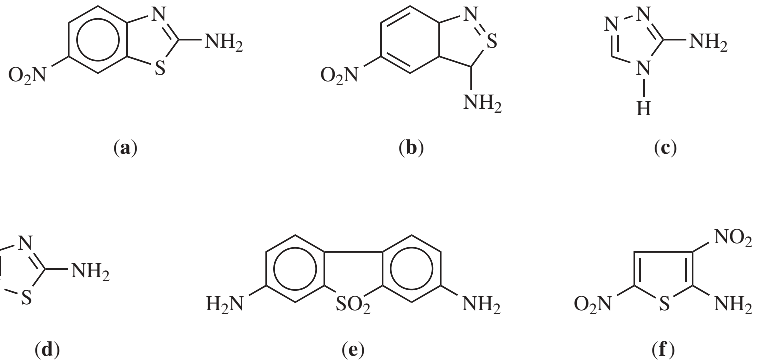


**Fig. 1.** Heterocyclic amines used in azo dyes. (**a**) 2-Amino-6-nitrobenzothiazole [6285-57-0]; (**b**) 3-amino-5-nitro-2,1-benzisothiazole [14346-19-1]; (**c**) 3-amino-4*H*-1,2,4-triazole [65312-61-0]; (**d**) 5-amino-1,2,4-thiadiazole [7552-07-0]; (**e**) 4,4′-diamino-2,2′-biphenylsulfone [6259-19-4]; (**f**) 2-amino-3,5-dinitrothiophene [2045-70-7].

rapidly and 2-chlorothiazoles are formed. When aminothiadiazoles (5-amino-1,2,4-thiadiazoles and 2-amino-1,3,4-thiadiazoles) are treated with sodium nitrite in phosphoric acid solution, diazonium salts are the products. These exhibit a higher coupling reactivity compared to diazotized 2,4-dinitroaniline (9). Among the various types of heterocyclic amines, it is evident that nitrosoamines are favored under dilute acid conditions and diazonium formation is favored under strong acid conditions. Diazotization is improved by the addition of a mixture of concentrated acetic acid and propionic acid (10). Further methods of diazotization of aromatic amines have been described (11,12).

Diazotizations in organic solvents followed by coupling or simultaneous diazotization and coupling in one step have gained importance (13). The process can be conducted batchwise or continuously. When the dye is soluble in the reaction mixture, the product can be packed out in its entirety. This offers an advantage in reducing the loss of dye during processing. The liquid dye also offers ease of handling, accuracy of measurement, and uniformity. Besides sodium nitrite [7632-00-0] and nitrosylsulfuric acid, nitrites of glycol and glycol derivatives (14) can be employed as diazotizing agents. These compounds in comparison to nitrites of low molecular weight alcohols, such as amyl nitrite, are much less dangerous in handling, physiological properties, and explosiveness. These types of processes have been employed for a limited number of commercial azo dyes. The mechanism of the diazotization reaction has appeared (15) and other results have been reviewed (16,17). Nitrosation of the amino group is the rate determining step; transformation to the diazonium ion follows:

$$\begin{aligned} &\mathrm{ArNH_2} + \mathrm{HNO_2} \longrightarrow \mathrm{Ar\overset{+}{N}H_2{-}NO} \longrightarrow \mathrm{ArNH{\cdot}NO} \longrightarrow \\ &\qquad \mathrm{ArN{=}N{-}OH} \longrightarrow \mathrm{Ar\overset{+}{N}{\equiv}N} \longrightarrow \mathrm{ArN{=}N^{+}} \end{aligned} \tag{3}$$

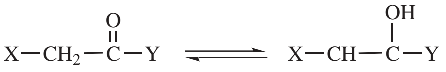
Before coupling, excess nitrous acid must be destroyed. Nitrite can react with coupling components to form nitroso compounds causing deliterious effects on the final dyestuff. The presence of nitrite can be detected by 4,4′-diamino-diphenylmethane-2,2′-sulfone [10215-25-5] (Green reagent) or starch–iodide. Removal of nitrite is achieved by addition of sulfamic acid or urea [57-13-6], however, sulfamic acid [5329-14-6] has been more effective in kinetic studies of nine nitrous acid scavangers (18).

$$\mathrm{NH_2SO_3H + HNO_2 \longrightarrow N_2 + H_2SO_4 + H_2O} \tag{4}$$

$$\mathrm{NH_2CONH_2 + HNO_2 \longrightarrow N_2 + NH_2COOH + H_2O} \tag{5}$$

**2.2. Azo Coupling.** The coupling reaction between an aromatic diazo compound and a coupling component is the single most important synthetic route to azo dyes. Of the total dyes manufactured, about 60% are produced by this reaction. Other methods include oxidative coupling, reaction of arylhydrazine with quinones, and oxidation of aromatic amines. These methods, however, have limited industrial applications.

All coupling components used to prepare azo dyes have the common feature of an active hydrogen atom bound to a carbon atom. Compounds of the following types can be used as azo coupling components: (*1*) aromatic hydroxy compounds such as phenols and naphthols; (*2*) aromatic amines; (*3*) compounds that possess enolizable ketone groups of aliphatic character, ie, compounds that have active methylene groups, where X is an electron attracting group such as –COR, –COOH, –CN, R is alkyl or aryl, and Y is usually a substituted or unsubstituted amino group;



$$X-CH_2-\overset{\overset{O}{\|}}{C}-Y \rightleftharpoons X-CH-\overset{\overset{OH}{|}}{C}-Y$$

and (*4*) heterocyclic compounds such as those containing pyrrole [109-97-7], indole [120-72-9], pyridine [110-86-1], pyrimidine [289-95-2], and similar ring systems, eg, 5-pyrazolones.

Analogous to aromatic halogenation, nitration, and sulfonation, the azo coupling reaction is an electrophilic aromatic substitution. The effect of the reaction rate of substituents on both the diazo and the coupler components is in agreement with this mechanism. Thus the reaction is facilitated by electron-attracting groups in the diazo components, and by electron-donating groups in phenol and aromatic amine-type coupler components. The reactivity of coupling components (nucleophilic substrate) increases with increasing basicity. The phenoxide ion ($ArO^-$) and free amine ($ArNH_2$) are more basic than corresponding free phenol and the ammonium ion ($C_6H_5NH^+{}_3$) and, therefore, react more easily. A mechanistic explanation of this acid–base equilibria has been discussed (19). The effect of pH on the coupling reaction changes from one set of conditions to another. In the case of the coupling of a simple benzenediazonium salt to a naphtholsulfonic acid whose hydroxyl group has a $pK_a$ of 9.0 at pH below 8, an increase in alkalinity by one pH unit increases the coupling rate tenfold because of the increase in the concentration of naphtholate anion. Above pH 10, the naphthol–naphtholate equilibrium is shifted completely to the right and the coupling rate is independent of hydroxyl ion concentration. However, at high pH the diazonium–diazotate equilibrium is involved and the rate of coupling declines because the diazotate does not couple. Therefore, an optimum pH exists for each azo coupling reaction that is limited by the acidities, expressed in pH units, that correspond to the $pK_a$ value of the coupling component or the constants of the diazonium–diazotate equilibria. This optimum pH range lies approximately between pH 4 and pH 8 for aromatic amines as couplers; for enols, eg, acetoacetanilide [102-01-2], 3-methyl-1-phenyl-5-pyrazolone [89-25-8], and phenols, the range is pH 7–9 and pH 9–10, respectively.

The role played by coupling components is somewhat more complex. Electron-attracting α-substituents, eg, acetoacetanilide, 5-pyrazolones, speed the coupling reaction of methylene compounds in alkaline media. On the other hand, the presence of groups, such as nitro and sulfonate, depress the coupling capability of phenols and aromatic amines. Electron-attracting groups promote the shifts of the phenol–phenolate anion equilibrium to the side of the reactive phenolate species; however, the lowering of electron density on the aromatic ring at the reaction site is the overriding factor. Thus nitronaphthols, in which both substituents are in the same nucleus, do not, or only very sluggishly, couple. This is especially true of nitrophenols. A technically important example is salicyclic acid, in which the effect of the carboxyl group on the $\pi$-electrons of the ring and the lower acidity of the phenolic proton because of hydrogen bonding, are responsible for depressing the ability to couple. On the other hand, since electron-donating groups such as alkyl, alkoxy, and amino residues, facilitate reaction, the second hydroxyl group of resorcinol enables this component to be used for syntheses that could not be carried out with phenol. Normally, coupling occurs at the position para to the hydroxyl group. If this is occupied by a substituent not readily eliminated, as in *p*-cresol [1319-77-3] or 2-naphthol [135-19-3], the diazo component attacks the ortho position. When both ortho and para positions are free, two arylazo residues can be introduced, but with phenols the second coupling occurs with great difficulty. A few well-known coupling components are shown in Figure 2 together with the favored positions of coupling under the conditions normally used. The complete ionization of sodium sulfonate groups in aqueous solution, as in H-acid [90-20-0] (**6**), decisively influences solution properties, and particularly the dyeing behavior of such compounds.

In coupling there are always two competing reactions:

$$\mathrm{Ar{-\!\!-}N_2^+X^- + RH \longrightarrow Ar{-\!\!-}N{=\!\!=}N{-\!\!-}R + HX} \tag{2}$$

$$\mathrm{Ar{-\!\!-}N_2^+X^- + HOH \longrightarrow Ar{-\!\!-}OH + N_2 + HX} \tag{6}$$

where Ar is an aryl radical, RH a coupling component, and $X^-$ a halide ion. Factors that increase the rate of the desired reaction (eq. 2) also increase the rate of diazo decomposition (eq. 6). Since the rates of the two reactions do not parallel each other, the yield of equation 2 can be maximized by a judicious choice of conditions.

Increasing the temperature of the coupling reaction usually has an unfavorable effect because the diazo decomposition reactions have greater energies of activation and hence larger temperature gradients than azo coupling. For every 10°C rise in temperature, the rate of coupling increases 2.0–2.4 times, whereas that of the decomposition rises 3.1–5.3 times.

The acid–base equilibria are fundamental to the kinetics of azo coupling and of practical significance for azo technology. Thus it is important that coupling reactions be carried out in a medium such that the acid–base equilibria of the diazo and coupling components favor as much as possible the diazonium ions and the phenolate ions or the free amine, respectively.

Broad principles governing the activity of coupling components may be summarized as follows:

1. Diazo coupling follows the rules of orientation of substituents in aromatic systems in accordance with the mechanism of electrophilic aromatic substitution and the concept of resonance.
2. Generally, phenols (as the phenolate anion) couple more readily than amines, and members of the naphthalene series more readily than the members of the benzene series.

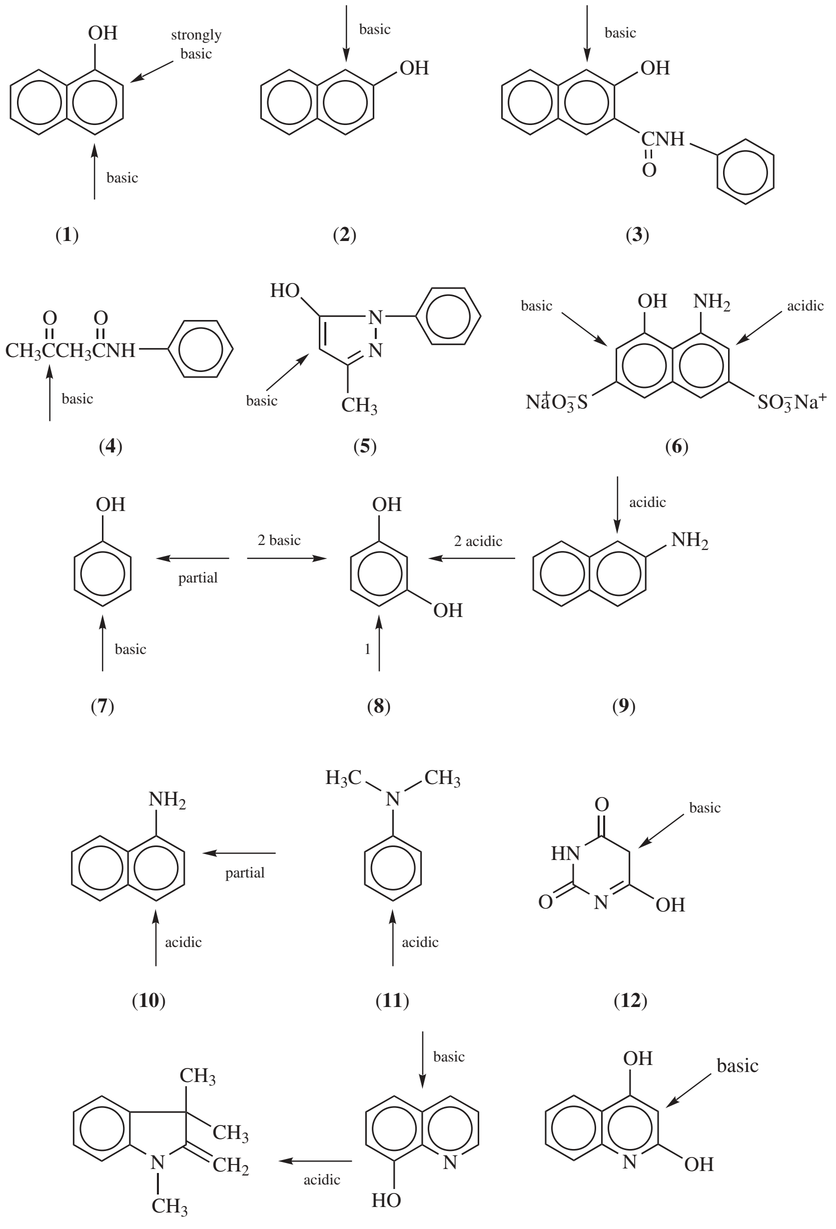
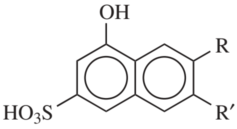


**Fig. 2.** Coupling components in azo dyes. The preferred positions of coupling are indicated by arrows and the usual pH conditions are noted. (**1**) 1-Naphthol [90-15-3]; (**2**) 2-naphthol [135-19-3]; (**3**) 3-hydroxy-2-naphthanilide [92-77-3]; (**4**) acetoacetanilide [102-01-2]; (**5**) 3-methyl-1-phenyl-5-pyrazoline [89-25-8] (enol form); (**6**) 8-amino-1-naphthol-3,6-disulfonic acid [90-20-0] (H-acid); (**7**) phenol [108-95-2]; (**8**) resorcinol [108-46-3] (1 and 2 indicate the first and second substitution sites); (**9**) 2-naphthylamine [91-59-8]; (**10**) 1-naphthylamine [134-32-7]; (**11**) *N,N*-dimethylaniline [121-69-7]; (**12**) barbituric acid [67-52-7]; (**13**) Fischer's base [118-12-7]; (**14**) 8-hydroxyquinoline [148-24-3]; (**15**) 2,4-dihydroxyquinoline [86-95-3].

3. Electron-attracting substituents in the coupling components such as halogen, nitro, sulfo, carboxyl, and carbonyl, are deactivating and tend to retard coupling.
4. A lower alkyl or alkoxy group substituted in the ortho or meta position to an amino group may promote coupling. Good couplers are obtained from dimethylaniline when lower alkyl, lower alkoxy, or both groups are present in the 2- and 5-position.
5. It is possible for diazo compounds to attack both the ortho and para position of hydroxyl and amino coupling components when these positions are not already occupied.

Technologically, the most important examples of such couplers are 1-naphthylamine, 1-naphthol, and sulfonic acid derivatives of 1-naphthol (Fig. 2). Of great importance in the dyestuff industry are derivatives of 1-naphthol-3-sulfonic acid, such as H-acid (8-amino-1-naphthol-3,6-disulfonic acid [90-20-0]) (**6**), J-acid (6-amino-1-naphthol-3-sulfonic acid [87-02-5]) (**16**), and gamma acid (7-amino-1-naphthol-3-sulfonic acid [90-51-7]) (**17**).



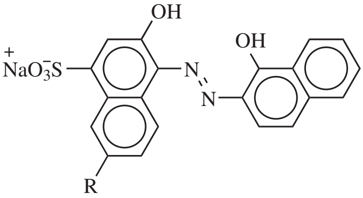
(**16**) $R = H, R' = NH_2$
(**17**) $R = NH_2, R' = H$

The ortho:para isomer ratio depends on several factors, including the nature of the diazo component, the nature of the solvent, the pH of the medium, the temperature of coupling, the presence of catalysts, and the position of substituents. Simple benzenediazonium compounds couple to 1-naphthol almost exclusively in the para position under acidic and weakly alkaline conditions; however, in strongly basic media considerable quantities of the 2,4-disazo dye are formed (20).

The ratio between the isomers obtained in coupling with 1,3- and 1,5-naphtholsulfonic acids depends on the reactivity of the diazo component. Energetic ones, such as the 2,4-dinitrobenzenediazonium compound, essentially couple only with 1-naphthol-3-sulfonic acid [3771-14-0] in the para position, but 4-chloro-benzenediazonium salt (a weaker diazo) attacks the ortho position. Both isomers result when mononitrobenzenediazonium compounds are used. The tendency to couple para is greater in 1-naphthol-5-sulfonic acid [117-59-9], $C_{10}H_8O_4S$ (21). For the combination of 2-nitrobenzenediazonium salt and 1-naphthol-3-sulfonic acid an increase in temperature from 10, to 20 and 30°C increases the ortho:para ratio from 3.2 to 4.35 and 7.55 (22). In one kinetic study, the azo coupling of gamma acid with strongly electrophilic diazo components such as 3-trifluoromethyl- and 4-nitrobenzenediazonium ion in concentrated aqueous alkaline solutions gave ratios of aminoazo to hydroxyazo compounds, which are much higher than expected on the basis of pre-equilibria (23). Relative increase of the aminoazo dyes in an alkaline system is attributed to a micromixing effect. The same effect is observed when a benzenediazonium ion is coupled with 5-hydroxy-2-naphthalenesulfonic acid [6500-22-4] (a stronger nucleophile than gamma acid) and a considerable amount of 5-hydroxy-6,8-bisphenylazo-2-naphthalene sulfonic acid is formed (24). Different solvents can affect azo coupling in different ways (25). The coupling of benzenediazonium tetrafluoroborate [446-46-8] with 2-naphthol is very rapid when the solvent system is changed from water to acetonitrile (26).

The azo coupling reaction proceeds by the electrophilic aromatic substitution mechanism. In the case of 4-chlorobenzenediazonium compound with 1-naphthol-4-sulfonic acid [84-87-7], the reaction is not base-catalyzed, but that with 1-naphthol-3-sulfonic acid and 2-naphthol-8-sulfonic acid [92-40-0] is moderately and strongly base-catalyzed, respectively. The different rates of reaction agree with kinetic studies of hydrogen isotope effects in coupling components. The magnitude of the isotope effect increases with increased steric hindrance at the coupler reaction site. The addition of bases, even if pH is not changed, can affect the reaction rate. In polar aprotic media, reaction rate is different with alkyl-ammonium ions. Cationic, anionic, and nonionic surfactants can also influence the reaction rate (27).

Diazophenols, ie, *o*-hydroxyaryldiazonium salts, couple to 1-naphthol in weakly basic solution primarily in the para position, but as the hydroxyl ion concentration is increased, formation of the ortho isomer is favored and is frequently the sole product. Pyridine and pyridine derivatives, urea, and acetate, etc, used as buffers can also catalyze azo coupling reactions (28). 1-amino-2-naphthol-4-sulfonic acid [116-63-2] (1,2,4-acid) and 1-naphthol yield the important Eriochrome Black A [3564-14-5] (**18**a, R = H) (CI Mordant Black 3; CI 14640) which is reportedly (20) a mixture of ortho and para isomers.

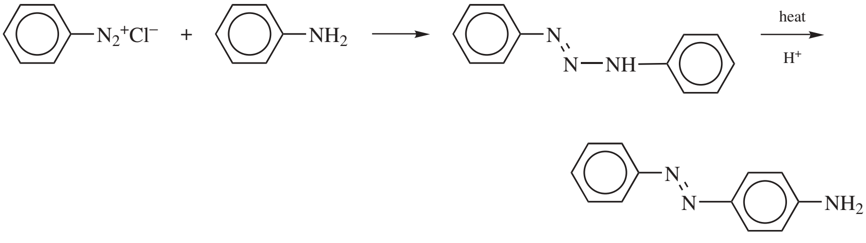


(**18**)

The corresponding diazo component with a 6-nitro substituent gives Eriochrome Black T [1787-61-7] (**18**b, R = $NO_2$) (CI Mordant Black 11; CI 14645) which is supposed to consist almost exclusively of the ortho compound.

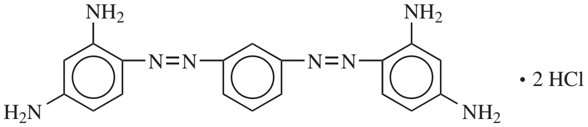
1,5-Dihydroxynaphthalene [83-56-7] behaves similarly to 1-naphthol; coupling takes place mainly in the 4-position by simple diazonium compounds, and in the 2-position with diazophenols. Diazotized 2-aminophenol-4-sulfonic acid [98-37-3] couples with 1,5-dihydroxynaphthalene to produce the important mordant dye Diamond Black PV [2052-25-7] CI Mordant Black 9; CI 16500).

6-Nitro-1-diazo-2-naphthol-4-sulfonic acid prefers the 2-position in spite of the nitro group, and increasing alkalinity favors ortho coupling with diazophenols. 1-Naphthalenesulfamic acid [24344-19-2] ($ArNHSO_3H$) and *N*-nitro-1-naphthylamine [4323-69-7] ($ArNHNO_2$) couple exclusively in the para position. The substitution of resorcinol [108-46-3] and *m*-phenylenediamine [108-45-2] is complicated and has been discussed (29,30). The first azo dyes from aniline, eg, Aniline Yellow [60-09-3] (**19**) (CI Solvent Yellow 1; CI 11000) were manufactured in 1861 and Bismark Brown [10114-58-6] (**20**) (CI Basic Brown 1; CI 21000) appeared in 1863. The reaction is as follows:



(**19**)

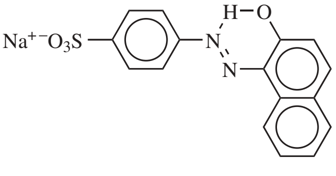
The dye (**19**) has little value for dyeing any textile fiber, but it is still manufactured for use as a diazo component for disazo dyes. In this type of reaction it is more usual to block the amino group, eg, by substituting anilinomethanesulfonic acid [103-06-0], $C_6H_5NHCH_2SO_3H$ for the aniline; the coupling then occurs exclusively in the position para to the amino group, and the sulfomethyl group is hydrolyzed giving the free amine. CI Basic Brown I is a disazo dye manufactured by adding two moles of sodium nitrite to three moles of *m*-phenylenediamine in a solution containing an excess of hydrochloric acid. The product is a mixture of aminoazo compounds, but the main component is (**20**).



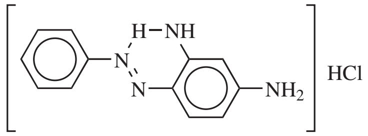
(**20**)

*Alkaline Coupling Process.* Orange II [633-96-5] (21) (CI Acid Orange 7; CI 15510), a monoazo dye discovered in 1876, serves as an example of the production of an azo dye by alkaline coupling. A suspension of diazotized sulfanilic acid (0.1 mol) is added to a solution (cooled to about 3°C) of 14.4 g 2-naphthol dissolved in 15 g 30% sodium hydroxide, 25 g sodium carbonate, and 200 mL of water. The temperature should not be allowed to rise above 5°C. The reaction is heated until solution occurs and the dye is precipitated with 100 g sodium chloride. The mixture is cooled and filtered, and the product is dried.

*Acid Coupling Process.* On the other hand, Chrysoidine Y [532-82-1] (**22**) (CI Basic Orange 2; CI 11270) is an example of a dye produced by acid coupling. Aniline, 9.3 g, is diazotized and the diazo solution is added to a solution of 11 g *m*-phenylenediamine in 200 mL water; then the solution is made slightly acidic with hydrochloric acid. The reaction mixture is maintained with stirring until coupling is complete as indicated by spot test where, upon addition of an alkaline solution of 2-naphthol, there is no color change if the diazo is exhausted. The solution is warmed to about 60°C. A concentrated solution of salt is added (about 120 g). The reaction mixture is then allowed to cool and the dye is filtered and dried. Reddish brown water-soluble crystals are obtained.



(**21**)

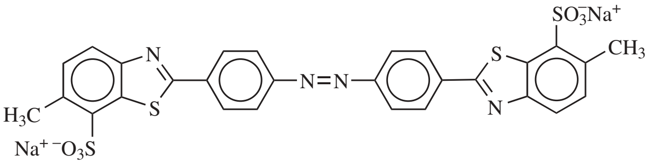


(**22**)

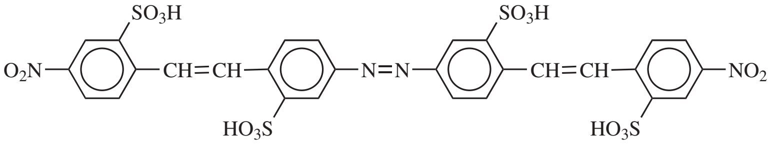
The dyes (**21**) and (**22**) were the first dyes manufactured by two separate reaction steps, ie, diazotization in one pot and the coupling reaction in another vessel, at BASF in 1875. Anthosin Orange 35 (BASF) is an Acid Orange 7 (**21**) listed along with 18 other commercial names in *AATCC Buyer's Guide* (31). The product is available in powder and concentrated liquid form. Its main application is for dyeing paper and to a lesser extent, leather and wool. Chrysoidine (**22**) is no longer an important cotton dye. For detailed information on azo coupling, mechanism, and properties of azo compounds, see references 32–36.

### 2.3. Other Routes to Azo Dyes.

*Oxidation of Aromatic Amines.* The technically important dye Direct Yellow 28 (**23**) [10114-47-3] (CI 19555) for cotton usage is manufactured by oxidation of dehydrothio-*para*-toluidinesulfonic acid sodium salt with sodium hypochlorite in aqueous alkaline solution.



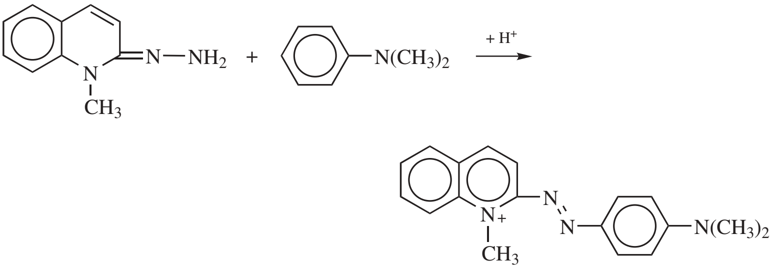
(**23**)



(**24**)

*Condensation of Nitro Compounds.* The stilbene dyes derived from condensation of 4-nitrotoluene-2-sulfonic acid [121-03-9] (para acid) in aqueous caustic solution either alone or with arylamines, are mixtures of dyes containing azo and azoxy groups with indefinite structures. The primary products are 4,4′-dinitro-2,2′-stilbenedisulfonic acid [128-42-7] and 4,4′dinitrodibenzyl-2,2′-disulfonic acid [6404-60-0] which condense further to form the dye. The properties of the stilbene dyes vary with the amounts and concentrations of the reactants and with the time and temperature of heating. The hue range is mostly yellow, orange, and brown, classified in the CI under stilbene dyes. The CI numbers in these cases refer not to any specific chemical structure, but to groups of commercial products which possess closely similar dyeing and fastness properties. A process was patented for making stable liquid directly using lithium hydroxide (37). Direct Yellow 11 [13253-77-3] (**24**) (CI 40000) is a stilbene dye sold under trade names such as Pontamine Yellow GXG (Mobay) or Fastusol Yellow 76 (BASF). The most probable structure is (**24**).

*Oxidative Coupling of Heterocyclic Hydrazones.* This method has opened the way to the preparation of azo derivatives of diazo compounds unobtainable by other means, ie, heterocyclic compounds in which the diazotizable amino group is conjugated with the heterocyclic nitrogen atom as in 2- and 4-aminopyridine, compounds which do not normally yield stable diazonium salts (38). The reaction occurs as illustrated by equation 7 for the interaction of (*N*-methylcarbostyryl)hydrazone [28219-37-6] and dimethylaniline; the overall process is oxidation.



(7)

The most suitable oxidizing agent is potassium ferricyanide, but ferric chloride, hydrogen peroxide in the presence of ferrous salts, ammonium persulfate, lead dioxide, lead tetraacetate or chromate, or silver and cupric salts may be useful. Water mixed, eg, with methanol, dimethylformamide, or glycol ethers, is employed as reaction medium.

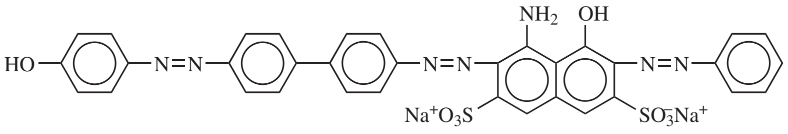
## 3. Classification

In addition to classification according to the number of azo groups, further subdivision is achieved, first according to whether the compound is water-soluble and, secondly, according to the types of component used. Another system of classification is based on dyeing classes. All colorants are divided to indicate the chief method of application or to indicate principal use. Azo dyes are found in the acid, basic (cationic), direct, disperse, mordant, and reactive dyeing classes. Although the two systems of classification overlap with each other, the chemical structure method is important from a chemistry viewpoint, whereas dyeing class method is important from an industrial viewpoint. In industry, a product can be offered competitively based on similar properties and function regardless of structure.

In the disazo group of azo dyes, primary and secondary types are distinguished. The former covers compounds made from two molecules of a diazo derivative and one molecule of a bifunctional coupling component. In both cases, the monofunctional reagent may consist of two molecules of one compound or one molecule of each of two substances used stepwise, the first alternative yielding symmetrical products. In stepwise reactions, it is the rule to carry out the coupling occurring with greater difficulty first (usually acid coupling), since generally when components contain one or more azo groups they become progressively more inert.

**3.1. Structural Representation.** To indicate the constitution of azo coloring matter in the conventional manner becomes much too cumbersome, particularly with polyazo dyes. Apart from using trade names, the color chemist has developed a kind of shorthand, which simultaneously provides some information about the synthesis of the azo compound concerned. A system of arrows is employed linking the intermediates used, the arrow pointing from the amino compound to be diazotized to the substance acting as the coupling component. With polyazo compounds, numbers show the order in which the processes are carried out and it is usually indicated whether the reaction is performed in acidic or basic solution when aminohydroxyl compounds are used as coupling components. For example, Amidine Benzo Dark Green N [3626-28-6] (CI Direct Green 1; CI 30280) is simply written as follows:

$$\text{phenol} \xleftarrow{3} \text{benzidine} \xrightarrow[\text{acid}]{1} \text{H}-\text{acid} \xleftarrow[\text{basic}]{2} \text{aniline}$$



The *Chemical Abstract Index* name is 2,7-naphthalene-disulfonic acid, 4-amino-5-hydroxy-3-[[4′-[(4-hydroxyphenyl)azo][1,1′-biphenyl]-4-yl]azo]-6-(phenylazo)-, disodium salt.

*Primary Disazo Dyes.* The following dyes are examples of the four types of primary disazo compounds. Their structures appear in Figure 3.

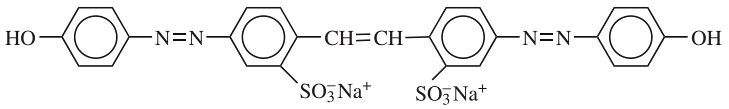
Fastusol Yellow 66 [91-34-9] (25) (CI Direct Yellow 4; CI 24890) is a symmetrical primary disazo dye from a tetrazo component (4,4′diamino-2,2′stilbenedisulfonic acid [81-11-8].

Amidine Fast Red F [2429-84-7] (26) (CI Direct Red 1; CI 22310) is an unsymmetrical primary disazo dye from a tetrazo component (benzidine [92-87-5]).

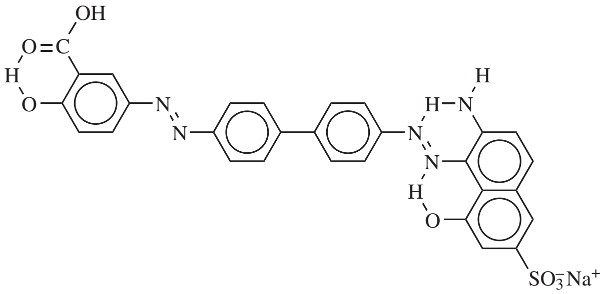
Resorcine Brown R [5850-16-8] (27) (CI Acid Brown 14, CI 20195) is a symmetrical primary disazo dye with bifunctional coupling component (resorcinol).

Calcocid Blue Black Ex [1064-48-8] (28) (CI Acid Black 1; CI 20470) is an unsymmetrical primary disazo dye with bifunctional coupling component (H-acid).

*Secondary Disazo Dyes.* There are about 250 dyes of known constitutions in this group. They are made by diazotizing an aminoazo compound, the amino group of which derives from the original coupling component and coupling



(**25**)



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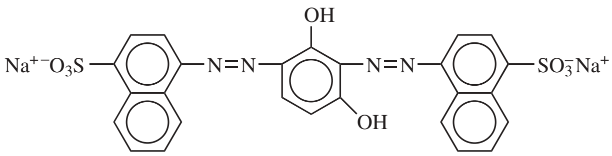

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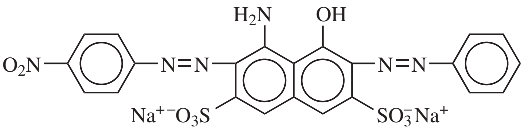
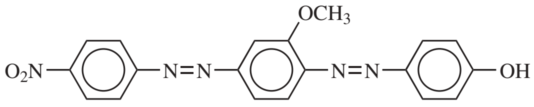


(**28**)

**Fig. 3.** Primary disazo dyes.

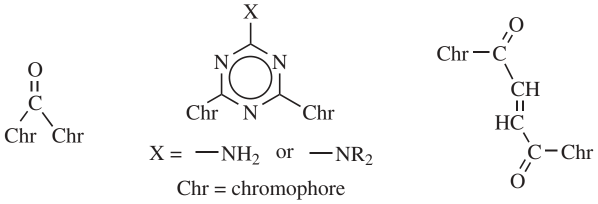
it to a suitable intermediate. Intrasil Orange YBLH [19800-42-1] (CI Disperse Orange 29; CI 26077) is an example as follows:

$$p\text{−nitroaniline} \longrightarrow o\text{−anisidine} \longrightarrow \text{phenol}$$



Sulphocyanone 5R [3351-05-1] (CI Acid Blue 113; CI 26360) (see structure **41**) is another example.

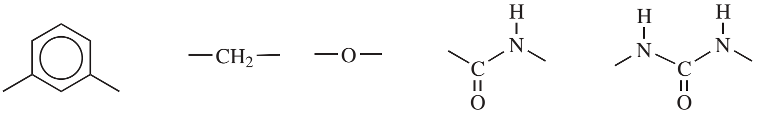
*Miscellaneous Disazo Dyes.* Another group of disazo dyes is prepared by condensation of two identical or different aminoazo compounds commonly with phosgene, cyanuric chloride, or fumaryl dichloride, the fragments of which act as blocking groups between chromophores.



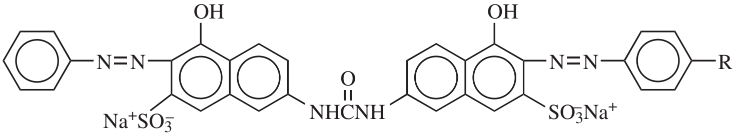
$X = -NH_2$ or $-NR_2$

Chr = chromophore

Other common blocking groups are



In this way, many green azo dyes have been made by combining separate conjugated systems in the same molecule, eg, one yellow and the other blue. The blocking or the insulating group prevents the electronic interaction of one chromophore system with the second. Chloramine Fast Scarlet 4BS [3441-14-3] (**29**) (CI Direct Red 23; CI 29160) and Fastusol Orange 85 [6420-41-3] (**30**) (CI Direct Orange 102; CI 29156) are examples.



(**29**) R = NHCOCH3
(**30**) R = COONa

*Trisazo and Polyazo Dyes.* These are mostly direct dyes, the hues are predominantly brown, black, or dark blue or green. Some are leather dyes. Benzidine, which used to be an important bisdiazo component, has been replaced by 4,4′-diaminobenzanilide [785-30-8], 4,4′-diaminodiphenylamine-2-sulfonic acid [119-70-0], etc. Benzidine dyes are almost never produced any longer because of their carcinogenicity. A triszazo dye, CI Direct Black 166 [57131-19-8], CI 30026 can be represented as follows:

$$m\text{-phenylenediamine} \xleftarrow{3} 4,4'\text{-diaminobenzanilide} \xrightarrow[\text{acid}]{1} \text{H-acid} \xleftarrow[\text{alk}]{2} \text{aniline}$$

CI Direct Black 22 [6473-13-8] (CI 35435) is an example of a tetrakisazo dye, (4,4′-diaminodiphenylamine-2-sulfonic acid bisdiazotized and coupled to 2 mol gamma acid; which is then bisdiazotized and coupled to 2 mol *m*-phenylenediamine).

## 4. Reactivity of Azo Dyes

This section is a distillation of progress made in the last few years on the degradation of azo dyes via oxygen-atom transfer, electron transfer, catalysis and radical routes. Exciting progress has been made possible by the application of the pulse radiolysis technique to dyes and by rigorous kinetic analysis. It addresses the underlying principles that govern the chemical reactivity of azo dyes. It sets a framework for providing an understanding of dye degradation in following areas of practical importance: (*1*) the fading of textiles dyes that occurs on laundering or on exposure to sunlight, and (*2*) potential mechanisms for the destruction of azo dyes produced in wastewater as a bi-product of textile dyeing and finishing processes.

The ultimate aim of recent research in these areas was to generate new routes to combat fading and, since conventional methods have limited success, to find new ways of treating dyes in waste streams.

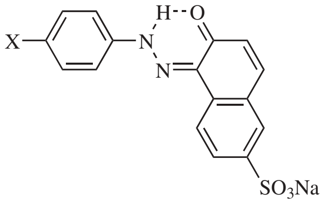
The major driver has been domestic laundering, where wash temperatures have become systematically lower over the last two decades due to the need for energy conservation. There has also been a general increase in colored textiles arising from the increased incidence of synthetic fibers, new applied textile finishes and fiber blends. This lowering in temperature has signaled the development of new low temperature bleaches to maintain stain removal and general whiteness of articles; the new bleaches also inhibit the transfer of dyes from one garment to another during the wash process by oxidizing the fugitive dye. One consequence of this trend has been an increased incidence of dye fading of colored garments in certain sectors of the marketplace. This has arisen as there is less of a tendency for consumers to separate colored and non-colored articles in washes *at low temperatures* in Europe, particularly evident in the UK. This trend, coupled with a desire for high efficiency cleaning, has led to the use of heavy-duty detergents containing bleach rather than the alternative color detergents that do not contain bleach. In the U.S., detergent formulations had been traditionally bleach-free, with consumers disposed to using bleach adjuncts separately from the main wash; however, this has also changed with the introduction of new low temperature bleaches in main wash formulations.

The relentless move in the dyeing industry towards reactive dyes for cellulosic fibers in recent years has exacerbated problems: (*1*) the relatively low fixation of reactive dyes onto cellulosic fibers compared to conventional direct dyes has led to much greater color discharge into dyehouse effluent, and (*2*) the widespread use of reactive dyeing trichromies that combine red, blue and yellow dyes to produce the desired color creates another issue; interaction with aggressive bleaches can induce color changes, which can be more perceivable than straightforward fading, ie, trichromies are more sensitive to shade changes on oxidation–reduction.

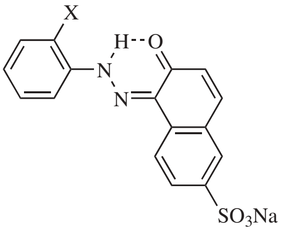
Until recently, progress on elucidating dye reactivity was not forthcoming due to the complexity of commercial dyes and their poor characterization either in solution or on surfaces. However, this has changed with the synthesis of a series of water-soluble model dyes and with the recognition that they could reproduce the key properties of chromophores in commercial dyes both in solution and on surfaces (39,40). Even with aggregated or disperse dyes, reactivity tends to be governed by equilibrium levels of dye in solution; aggregated or insoluble dyes are inert. This is manifest by the observation of zero order decay kinetics (41). However, photofading of textile dyes is more complex as chemical groups on the textile surface may influence reaction pathways (42).

Nevertheless, even with model dyes, mechanistic work was still difficult to accomplish. For example, product analysis of dye oxidation products, a key weapon in understanding mechanisms was of limited value due to a multiplicity of small reaction products, arising from intermediates being more readily oxidized. Thus, emphasis was placed upon investigating the early stages of the reaction to elucidate mechanistic information. This involved; (*1*) use of head space analysis to "trap" and detect volatiles unable to participate in further reaction, (*2*) kinetic studies to determine the rate controlling step, and (*3*) use of pulse radiolysis to follow formation and decay of intermediates formed in initial stages; a productive and fruitful technique in studying electron transfer and radical reactions.

Key to the elucidation of the mechanism of oxidation was the synthesis and characterization of a series of substituted arylazonaphthol dyes *para* (**31a**), *ortho* (**31b**) that mimic typical commercial dye chromophores, and a systematic kinetic investigation of their oxidation in aqueous solution.



(**31a**)



(**31b**)

In this way, mechanistic information became accessible that would otherwise have been difficult to obtain for commercial dyes, particularly on fabrics and placed mechanistic understanding of fading of dyes on a sound footing: (*1*) mechanistic information was obtained from model dyes that would otherwise be difficult, due to commercial dyes and/or dyes bound to textiles being poorly characterized, (*2*) pitfalls in kinetic analyses that are so prevalent in the literature could be avoided, and (*3*) a central factor was the recognition that the mechanism of oxidation of a reactive dye, Remazol Red RB, bound to cotton is similar to that in homogeneous solution.

This section involves four main issues: (*1*) The reactive species responsible for oxidation or fading of dyes, (*2*) The site of attack, (*3*) The role of dye substituents or dye type in controlling oxidation, and (*4*) The mechanism of oxidation.

### 4.1. Key Dye Characteristics Influencing Oxidation.

*Dye Tautomeric Form and p$K_a$.* There are two important properties of dyes that are paramount in controlling their oxidation and these are discussed in this section. The first property to note is that reactivity of dyes is frequently controlled by one of its tautomeric forms. Indeed, dyes that adopt the hydrazone tautomeric form tend to be most sensitive to oxidation and are characterized by their deeper colors.

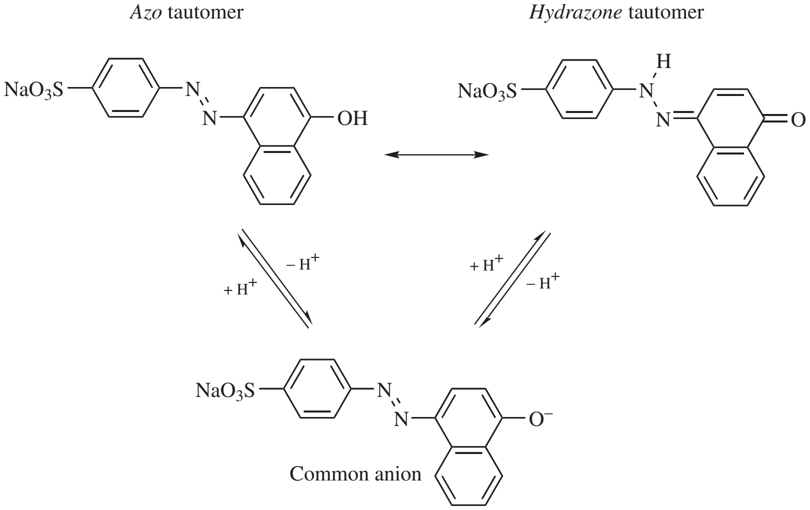


**Fig. 4.** Tautomeric equilibria in azo dyes.

Thus, it is commonly assumed that the hydrazone tautomeric form is the reactive dye species; this is a common misconception, as is shown below. However, dye tautomeric equilibria are of fundamental importance to oxidation/ reduction, thus the factors influencing tautomerism are discussed.

In particular, tautomeric equilibria are set up when there is a naphtholic hydroxyl group conjugated with the azo linkage. The equilibrium mixture of two tautomeric forms, *azo* or *hydrazone* forms, is illustrated for 1-arylazo-4-naphthol dyes in aqueous solution (Fig. 4).

These forms have characteristically different visible spectra: *azo* absorbing typically at 400–440 nm (yellow) and *hydrazone* at 475–510 nm (orange/red). When the hydroxyl group is located in the naphthol ring in a position *ortho* to the azo linkage, the *hydrazone* form predominates in aqueous media. In organic solvents (43), in micelles (44), on surfaces or bound to polymers (44) both forms can be detected, with the *azo* form favored, particularly with electron-releasing *para*-substituents (44). However, when the dye does not contain a hydroxyl group (or if it contains a phenolic hydroxyl group) the *azo* form predominates.

The second point to make is that the most important parameter that signifies the sensitivity of an azo dye to oxidation or reduction (39,40) is its p$K_a$, associated with the naphtholic hydroxyl group. Nevertheless, dye p$K_a$ values are rarely measured, despite the simplicity of measurement (39,40) but no doubt this will change with the recognition that it is a key indicator of susceptibility to oxidation–reduction. The literature is abound with papers that substituents *ortho* to the azo group protect the dye against oxidation; this is another misconception. Indeed, such *ortho* substituents influence the p$K_a$, which, in turn, governs oxidation.

Azo dyes containing naphtholic groups have p$K_a$ values in the region 8–12, which means they dissociate in alkaline media to form a common anion, so called

Table 1. **p$K_a$ Values for Substituted 1-Arylazo-2-Naphthol Dyes and Corresponding Rate Constants ($M^{-1}s^{-1}$) for Reaction with $HSO_5^-$ at pH 10.5/40°C**

| | *para-* | | *ortho-* | |
|---|---|---|---|---|
| Substituent | p$K_a$ | $k_2$ (obs), $M^{-1}s^{-1}$ | p$K_a$ | $k_2$ (obs), $M^{-1}s^{-1}$ |
| —H | 10.8 | 7.2 | 10.8 | 7.2 |
| —$CH_3$ | 10.9 | 10.8 | 11.4 | 1.6 |
| —$CH(CH_3)_2$ | 10.9 | 11.2 | 11.4 | 1.4 |
| —Cl | 10.5 | 9.6 | 11.3 | 0.42 |
| —$OCH_3$ | 10.8 | 16.5 | 11.7 | 0.29 |
| —$COCH_3$ | 10.9 | 6.5 | | |
| —$NO_2$ | 10.7 | 8.9 | 11.6 | 0.28 |
| —$CO_2^-$ | 11.2 | 3.2 | 12.2 | 0.20 |
| —$SO_3^-$ | 10.8 | 4.9 | 12.1 | 0.053 |

because it is common to both the azo and hydrazone forms. Although the negative charge is delocalized over the entire molecule, the common anion has predominantly *azo* character (45). Such equilibria are important since it is found that one of the dye forms tend to dominate reactivity. Earlier, it was stated that a common misconception is that the *hydrazone* form is the reactive form. It will be shown that the common anion is normally the most reactive form. Indeed, it is $10^5$ times more reactive towards hypochlorite than the *hydrazone* form.

The influence of substituents on influencing dye p$K_a$ values is shown in Tables 1 and 2.

Table 1 illustrates the influence of dye substituents upon the p$K_a$ and shows that *para-* substituents have little influence upon dye p$K_a$, indicating that intramolecular hydrogen bonding plays a predominant role. On the other hand, *ortho-* substituents increase p$K_a$ values, partly by reinforcing hydrogen bonding, and it appears that charged substituents are most influential. Indeed, the carboxylate or sulfonate group increase the p$K_a$ from 10.8 to over 12. Inspection of Table 2 evidently illustrates that the effects are larger for 2-arylazo-1-naphthol dyes. This indicates that the presence of the *ortho* sulfonate in the *naphthol* ring- as well as in the *aryl* ring- also has some influence and p$K_a$ values in excess of 13 can be obtained.

Table 2. **p$K_a$ Values of Substituted 2-Arylazo-1-Naphthol Dyes and Corresponding Rate Constants ($M^{-1}s^{-1}$) for Reaction with HOCl at pH 10/40°C**

| Substituent | $k_2$ (obs), $M^{-1}s^{-1}$ | p$K_a$ |
|---|---|---|
| —H | 27.2 | 11.5 |
| *p*-$SO_3^-$ | 17.6 | 11.3 |
| *o*-$CH_3$ | 7.3 | 12.0 |
| *o*-Cl | 5.4 | 11.7 |
| *o*-$OCH_3$ | 2.9 | 12.5 |
| *o*-$CO_2^-$ | 0.84 | 13.2 |
| *o*-$SO_3^-$ | 0.17 | 13.2 |

*Kinetic Investigations of Dyes. Reactively Bound to Textiles.* The fading of a covalently-bound reactive dye on textiles due to domestic washing can result from: (*1*) (Per)hydrolysis of the reactive links, which may predominate for bleach-insensitive dye chromophores at high wash temperatures. (*2*) Abrasive loss, particularly of, but by no means limited to, prints; this arises from mechanical action and may be the most important route in bleach-free detergent formulations. (*3*) Oxidative destruction of dye chromophores, the main pathway at low and medium wash temperatures with more active bleaches in the presence of sequestrants. (*4*) Metal catalyzed reactions.

Dye fading can be considered (46) to occur by a two-step model, which initially involves complexation between the two reactants, followed by reaction between them:

$$\text{Peracid} + \text{Dye} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{(C)}}{[\text{Peracid/Dye}]} \xrightarrow{k_r} [\text{Bleached dye}] \tag{8}$$

where $k_f$, $k_b$, are the formation and dissociation rate constants for complex C and $k_r$ is the bleaching rate constant.

For a second-order reaction, the rate of dye loss is given by:

$$-d[\text{Dye}]/dt = k_2\ [\text{Peracid}]\ [\text{Dye}] \tag{9}$$

where $k_2$ is the second-order rate constant.

Assuming steady-state in complex (C),

$$k_2 = k_f \cdot k_r/(k_b + k_r) \tag{10}$$

Normally, dye oxidation is rate determining, ie, $k_r < k_b$ thus:

$$k_2 = K_c k_r = k_2(\text{obs}) \tag{11}$$

where $K_c$ is the equilibrium constant for complexation. This shows that the oxidation rate depends not only upon the intrinsic reactivity, $k_r$, but also upon the extent of contact between oxidant and dye, $K_c$.

Rate constants for dye fading are lower than for bleaching in homogeneous solution primarily due to lower surface peracid levels ($K_c$), and requires repeat washing or higher peracid levels. Another key factor is that surfaces may not only influence the tautomeric form of dyes but also dye p$K_a$ values, particularly for noncovalently bound dyes. However, effects of substituents on fading rates of azo dyes (47) are similar to those for homogeneous bleaching, consistent with the finding (46) that homogeneous and heterogeneous mechanisms of oxidation of azo (or sulfur dyes) are correspondingly similar.

*Model Dyes in Solution.* To facilitate meaningful kinetic studies, it is essential to investigate small, highly soluble and well-characterized dyes that have structural motifs representative of commercial dyes. Dyes bound to textiles are poorly characterized and difficult to manipulate for kinetic studies; commercial dyes often contain high levels of impurities and have large, complicated structures, which lend them a tendency to aggregate in solution. Even in solution, dyes need to be examined at low concentrations and natural ionic strength to avoid the aggregation of dyes that occurs at higher ionic strength or in the presence of buffers. Addition of sequestrants is also necessary to remove the effects of the trace metals that tend to be associated with dyes and which can cause irreproducible behavior.

The principles of dye oxidation were determined from a comparative assessment of dye oxidation by hypochlorite, peracids and hydrogen peroxide.

**4.2. Oxidants Used as Detergent Bleaches.** The typical bleaches found in detergents or detergent adjuncts are sodium hypochlorite, peracids (formed *in situ* from precursors) and hydrogen peroxide.

*Hypochlorite.* The most aggressive and most efficient oxidant at low temperatures is hypochlorite. In fact, hypochlorite is so reactive that it is not used in detergent formulations but as a household bleach or as a bleach additive to whiten whites, particularly in emerging and developing markets. Nevertheless, it is highly reactive towards dyes and is capable of causing dye fading even via its use as a disinfectant in domestic water supplies (typically ~30 $\mu M$ hypochlorite) particularly in the U.S. or Japan.

The relevant equilibria governing speciation of hypochlorite are

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+ \qquad (pK_a = 3.3) \tag{12}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (pK_a = 7.5) \tag{13}$$

The active species for stain bleaching are aqueous chlorine ($pH < 4$) and undissociated hypochlorite (pH 4–10.5), which is a powerful electrophile due to the leaving group efficacy ($pK_a$) of hydrochloric acid. The ionized hypochlorite molecule $ClO^-$ is relatively unreactive to many stains/ microbes; indeed, $pH > 12$ are used to prolong the shelf-life of common household bleaches.

*Hydrogen Peroxide.* Hydrogen peroxide was first used as a bleach in detergents in Europe in 1908 and traditionally has been the main oxidant in detergents. It is normally incorporated in the form of sodium perborate or sodium percarbonate. The former hydrolyzes rapidly in water to liberate hydrogen peroxide whereas the latter is a true perhydrate, which instantly releases peroxide upon dissolution. Hydrogen peroxide is a safe, mild bleach, but is effective mainly at high temperatures. Its $pK_a = 11.6$ and the active oxidant for stain bleaching tends to be the perhydroxyl anion, $HO_2{}^-$.

*Peracids.* The move towards synthetic fabrics and colored wash loads in Europe, and the more conscious need for conservation of energy, has led to lower wash temperatures, at which hydrogen peroxide is a much less effective bleach. This has led to the development of more reactive peracids for detergent bleach applications. However, direct incorporation of peracids into detergent products has not proved possible to date due to incompatibility with detergent formulation ingredients, leading to the concept of activation of hydrogen peroxide with bleach precursors or activators. Generally, peracids are formed according to Fig. 5.

One example is TAED (tetraacetyl ethylene diamine) first introduced in Europe some 20 years ago; TAED reacts with $H_2O_2$ in the wash to form peracetic acid. The specific formation of peracetic acid from TAED is depicted in Fig. 6.

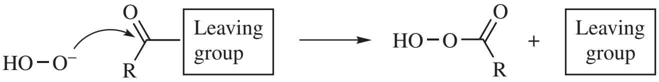
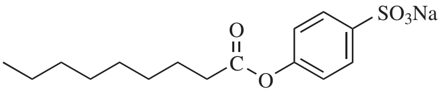


**Fig. 5.** Formation of peracid *via* perhydrolysis of precursors.

A further example, SNOBS (sodium nonanoyl oxybenzene sulfonate) (**32**) from which pernonanoic acid is generated, has later found application in the U.S.



(**32**)

The active species in bleaching of stains on fabrics is normally the undissociated peracid.

### 4.3. Oxygen-Atom Transfer Reactions.

*Kinetic Studies of Oxidation of Dyes with Detergent Bleaches.* Kinetic investigations of azo dye oxidation by typical bleaches are elegantly simple and facilitate identification of the reactive species. The rate law for decolorization of non-aggregating dyes by peracids, in the absence of interfering trace metals, is described by:

$$-d[D]/dt = k(\mathrm{obs})[D]_T = k_2(\mathrm{obs})[D]_T[PA]_T \quad (14)$$

where $[D]_T$ and $[PA]_T$ denote total concentrations of dye and peracid, respectively and $k$(obs), $k_2$(obs) are the observed, ie, pH dependent, first- and second-order rate constants, respectively.

Experimentally determined second-order rate constants were found to exhibit maxima with change in solution pH, with the maximum in rate occurring at a pH midway between the p$K_a$ of the dye and that of the peracid. This situation occurs only when the relevant rate equations are

$$-d[D]/dt = k_2^E[PA][D^-] = k_2^N[PA^-][HD] \quad (15)$$

where superscripts refer to electrophilic ($E$) and nucleophilic ($N$) reaction by peracid.

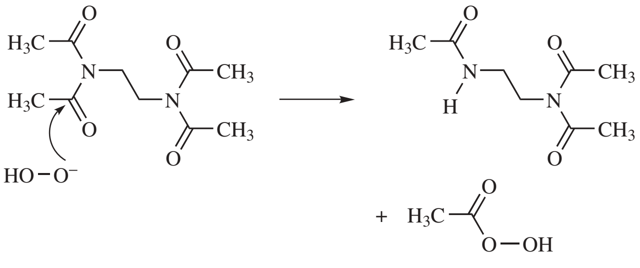


**Fig. 6.** Formation of peracetic acid *via* perhydrolysis of TAED.

The observed second-order rate constant, $k_2$(obs) can be expressed as follows:

$$\begin{aligned} k_2(\mathrm{obs}) &= k_2^E\{1/(1+K_A/[H^+]) \times 1/(1+[H^+]/K_D)\} \\ &= k_2^N\{1/(1+[H^+]/K_A) \times 1/(1+K_D/[H^+])\} \end{aligned} \tag{16}$$

where $K_A$ and $K_D$ are the acid dissociation constants for the peracid and dye, respectively.

Differentiation of both these expressions with respect to $[H^+]$ leads to a maximum value for $k_2$(obs) at a pH given by:

$$\mathrm{pH\ at\ } k_2(\mathrm{obs})_{\mathrm{MAX}} = \{\mathrm{p}K_a^{(PA)} + \mathrm{p}K_a^{(HD)}\}/2 \tag{17}$$

This analysis is important as it shows that the reaction proceeds *via one reactant that is dissociated and another that is undissociated*, ie, both are involved in the rate determining step. Although there are two possible ionic reactions that could contribute to the overall rates, only one reaction is significant in all cases. Furthermore, the rates strongly depend upon the leaving group character ($\mathrm{p}K_a$) of parent acids, implicating heterolytic peroxide bond scission in the transition state as the kinetically significant step. This suggests that *oxygen radicals are not involved in the initial stage of dye oxidation*. This is an important conclusion derived from an elegantly simple, noninvasive route that may not necessarily be derived from radical trap studies. For example, radicals may be involved in subsequent reaction steps or radical traps may react with oxidant. Overall, kinetic studies can provide valuable information about the reactants involved in the rate determining step and subsequent breakdown of the activated complex.

Although this analysis indicates that one reactive species is dissociated and the other undissociated, it does not permit unambiguous identification of reactive species. Nevertheless, in the work that follows, another key point emerges:

*The active oxidant is more often that not present in low concentrations, ie, is not the main solution species, which leads to interpretive pitfalls so prevalent in the literature.*

The observed maximum second-order rate constants for reaction of bleaches with substituted dyes are shown in the Tables 1–3. Initially restricting attention to second-order rates with peroxosulfate (Table 1). It is clear that the influence of *para*-substituent is small. In contrast, *ortho*- substituents have a marked effect, suppressing observed rates by 50–100 fold. The uncharged peracids, MCPBA and HOCl show the same trends as peroxosulfate, with *ortho*- substituents suppressing rates by 50-fold in both cases (Table 3). In line with effects on dye $\mathrm{p}K_a$ values, the largest effects are observed with substituted 2-arylazo-1-naphthol dyes (Tables 2 and 3).

On the other hand the maximum $k_2$(obs) values for hydrogen peroxide oxidation behave quite differently: the rate increases with *ortho*- substitution. Furthermore, observed rates do not become suppressed as the substituent increases in size or becomes charged. This suggests that hydrogen peroxide may function by a different mechanism from peracids.

Table 3. **Rate Constants ($M^{-1}s^{-1}$) for Reaction of Substituted 1-Arylazo-2-Naphthol Dyes with Various Oxidants at 40°C**

| *ortho*-Substituent | p$K_a$ | MCPBA $k_2$(obs) $M^{-1}s^{-1}$ (pH 10) | HOCl $k_2$(obs), $M^{-1}s^{-1}$ (pH 10) | $H_2O_2$ $k_2$(obs), $M^{-1}s^{-1}$(pH 11) |
|---|---|---|---|---|
| —H | 10.8 | 0.50 | 147 | 0.0020 |
| —$CH_3$ | 11.4 | | 52 | 0.0077 |
| —$CH(CH_3)_2$ | 11.4 | 0.087 | 68 | 0.0079 |
| —Cl | 11.3 | 0.044 | 35 | 0.026 |
| —$OCH_3$ | 11.7 | | 16 | 0.0061 |
| —$NO_2$ | 11.6 | | 8.5 | 0.042 |
| —$CO_2^-$ | 12.2 | | 2.9 | 0.0074 |
| —$SO_3^-$ | 12.1 | 0.011 | 3.8 | 0.030 |

If speciation of reactants are considered, then pH-independent second-order rate constants can be calculated from rate data, using eq. (16). Values for $k_2^E$ for hypochlorite oxidation are given in Table 4 for the *ortho*-substituted dyes and compared to those for corresponding *para*- substituents. Inspection of $k_2^E$ values show that they are remarkably similar to those for the corresponding *p*-substituted dyes, *ie*, there is no special effect of *ortho*- substituents. Similar rate constants are obtained from 2-arylazo-1-naphthol dyes. This is compelling evidence that hypochlorite acts as an electrophile, *despite the fact that the reactants are not the main solution species of peracid and dye.* This data suggests that the primary role of dye substituent is to shift the p$K_a$ of the dye, thereby changing the concentration of the common anion. A similar picture emerges for peracids (undissociated peracid reacts with ionized dye), but similar analyses indicate that hydrogen peroxide acts differently. In particular, *ortho*- substituents give similar rates to corresponding *para*- substituents only if the perhydroxyl anion and the *hydrazone* form of the dye are the active species.

An elegant confirmation that the common anion is highly reactive and the tautomeric form most likely to undergo reaction with peracids by electrophilic attack is provided using oxaziridines, which do not dissociate in aqueous media. Oxaziridines are a class of compounds having a heterocyclic ring comprising an oxygen, a nitrogen and a carbon atom that function as electrophilic

Table 4. **p$K_a$ Values of Substituted 1-Arylazo-2-Naphthol Dyes and Corresponding Rate Constants ($M^{-1}s^{-1}$) for Reaction with NaOCl at 40°C/pH 10**

| Substituent | $k_2$(obs), $M^{-1}s^{-1}$ | | p$K_a$ | | $k_2^E$, $M^{-1}s^{-1}$ | |
|---|---|---|---|---|---|---|
| | *para* | *ortho* | *para* | *ortho* | *para* | *ortho* |
| —H | 147 | 147 | 10.8 | 10.8 | 310,000 | 310,000 |
| —$CH_3$ | 158 | 52 | 10.9 | 11.4 | 450,000 | 420,000 |
| —$CH(CH_3)_2$ | 161 | 68 | 10.9 | 11.4 | 470,000 | 550,000 |
| —Cl | 157 | 35 | 10.5 | 11.3 | 190,000 | 230,000 |
| —$OCH_3$ | 196 | 16 | 10.8 | 11.7 | 410,000 | 250,000 |
| —$COCH_3$ | 51 | | 10.9 | | 150,000 | |
| —$NO_2$ | 62 | 8.5 | 10.7 | 11.6 | 110,000 | 110,000 |
| —$CO_2^-$ | 66 | 2.9 | 11.2 | 12.2 | 310,000 | 140,000 |
| —$SO_3^-$ | 92 | 3.8 | 10.8 | 12.1 | 220,000 | 150,000 |

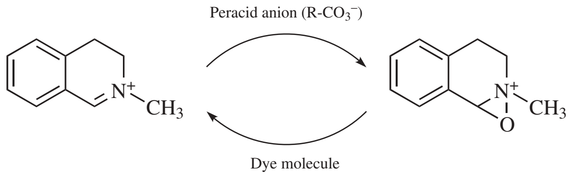


**Fig. 7.** Imine-catalyzed dye oxidation.

oxygen-atom transfer agents and are typically formed by reaction of an electron-deficient imine with a peracid, in particular with the peracid anion. Of particular interest is the oxaziridine salt formed from the *N*-methyl-1,2-oxo-3,4-dihydroisoquinolinium salt. This has been found to be a more effective oxygen-atom transfer agent than peracids. Organic catalysis of dye oxidation by imines *via* an electron-deficient oxaziridine is illustrated in Fig. 7.

Profiles for observed rate constants were found to follow speciation of the common anion, from which $k_2^E$ values of $0.5–1.2 \times 10^4$ $M^{-1}s^{-1}$ were obtained. These values are higher than those for typical peracids ($\sim10^2$ $M^{-1}s^{-1}$) but slightly lower than for hypochlorous acid ($\sim10^4$ $M^{-1}s^{-1}$). Overall, intercomparison of oxaziridine rate constants with other oxidants, peracids and hypochlorous acid is consistent with view that they all function as electrophiles and confirms that the common anion is a highly reactive form of the dye.

*Site of Initial Attack.* The initial site of attack can be pinpointed by examining the influence of judiciously placed dye sulfonate groups on reaction rates with negatively charged oxidants.

In particular, rate constants for 1-arylazo-2-naphthol dyes with $HSO_5^-$ are selectively suppressed (relative to HOCl) by *ortho*- sulfonate groups (48) in the aryl ring but not when placed in the naphthol ring. As $HSO_5^-$ is negatively charged, the contrast with HOCl suggests that charge-charge interactions play a key factor in reducing absolute rates, ie attack occurs on the negatively charged nitrogen atom of the common anion adjacent to the aryl ring.

In contrast, oxidation of 2-arylazo-1-naphthol dyes by the perhydroxyl anion give absolute rate constants that are an order of magnitude lower that the corresponding 1-arylazo-2-naphthol dyes (48). Evidently, the presence of the negatively charged *ortho*- sulfonate upon the naphthol ring of the hydrazone form of the dye plays a key role in suppressing rates. This does not happen when negatively charged substituents are placed in the aryl ring of 1-arylazo-2-naphthol dyes. As the perhydroxyl anion is negatively charged, this suggests that the imine carbon atom is the most likely site of attack in the hydrazone tautomer.

The reaction with chlorine in acidic media involves initial attack by the electrophilic chlorine molecule on the nitrogen atom containing the highest electron density, ie, upon the *N*-H nitrogen atom of the hydrazone tautomer of the dye. The mechanism is thought to involve nucleophilic attack by the nitrogen lone pair upon the chlorine molecule, resulting in heterolytic scission of the Cl-Cl bond, with expulsion of chloride and concomitant loss of a proton from the nitrogen atom (39,40).

*Mechanisms.* A plausible scheme (49) for reaction of chlorine with dye in acidic media is illustrated in Fig. 8. In essence, $Cl_2$ delivers a chlorine atom as $Cl^+$ which, upon subsequent hydrolysis, leaves as $Cl^-$, ie, a net two-electron reduction of $Cl_2$. A second molecule of $Cl_2$ may be utilized by rapid oxidation of the diazene intermediate to the diazonium salt by a similar mechanism; otherwise, the diazene will oxidise in air initially to form the diazene radical, which, in turn will liberate nitrogen (Fig. 8). Excess chlorine may be consumed by chlorination of the quinone ring.

A corresponding reaction (39,40) with inorganic or organic peracids in alkaline media is shown in Fig. 9, using hypochlorous acid as typical peracid oxidant.

A mechanism for the reaction of dye with hydrogen peroxide is illustrated in Fig. 10.

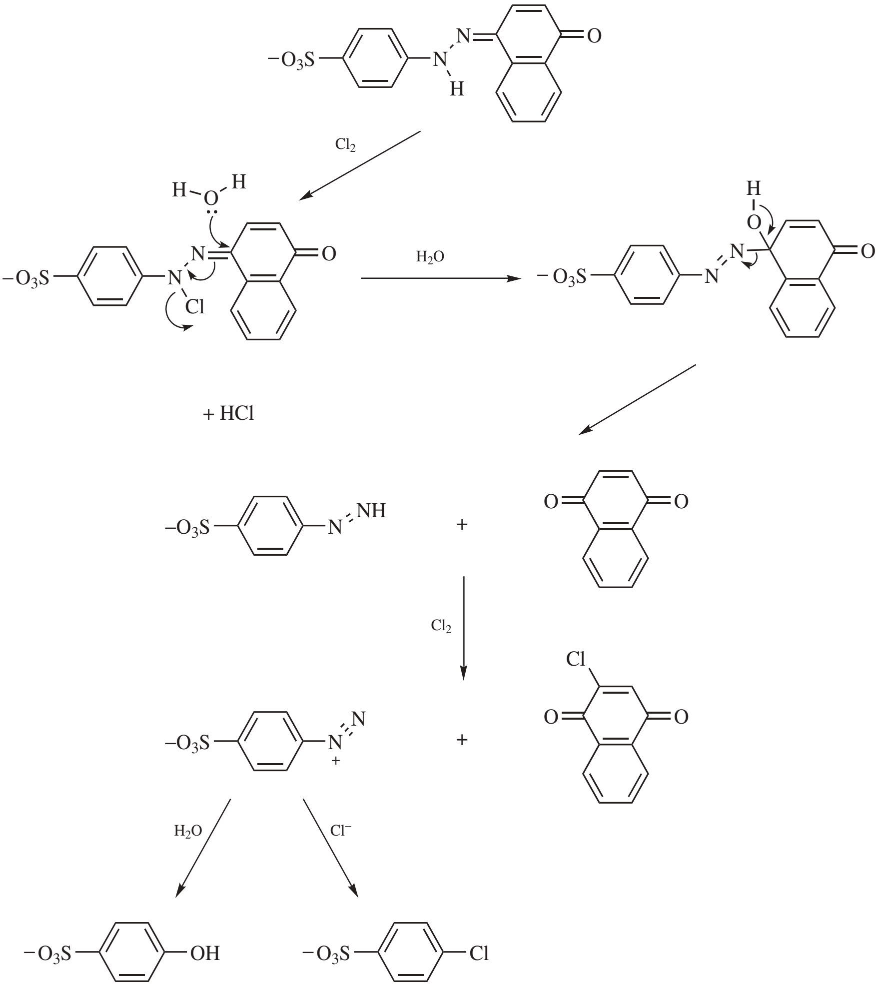


**Fig. 8.** Postulated reaction pathway for oxidation by $Cl_2$ in acid media.

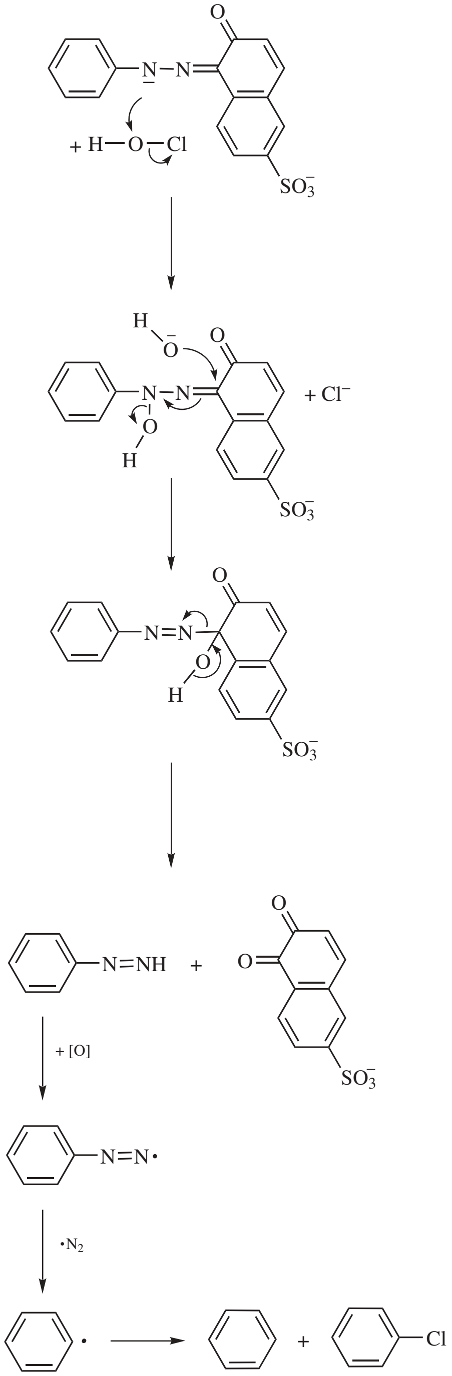


Fig. 9. Postulated reaction pathways for oxidation by HOCl in alkaline media.

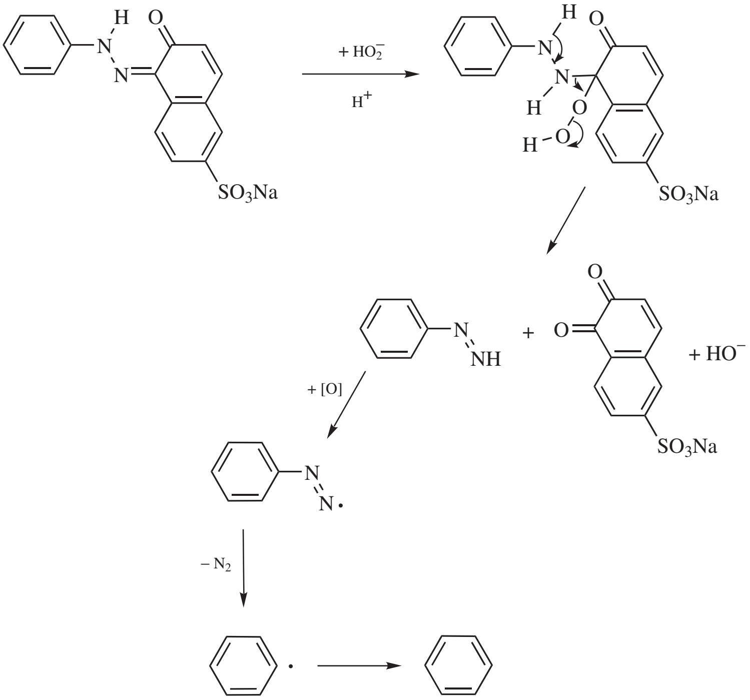


**Fig. 10.** Postulated reaction pathway for oxidation by hydrogen peroxide.

**4.4. Electron-Transfer, Reductive and Radical Reactions.** *Pulse Radiolysis.* Exciting progress has been made in this area, particularly using pulse radiolysis techniques. In the pulse radiolysis technique, pulses of ionizing radiations are used to generate radicals in the nanosecond timescale. It offers a simple, convenient, clean and efficient method for generating reactive radicals for selective and exclusive reaction with substrate (50). It is an excellent technique for studying the initial phases of reaction by detecting and following the fate of reaction intermediates.

Basically, the sample is subject to a radiolytic burst of electrons, eg, high energy electron beams from a linear accelerator or short pulses of fast electrons from a Van der Graaf generator. Unlike conventional spectroscopy where the solute is selected to sample electromagnetic radiation, the electron burst interacts with the medium to generate radical species, as illustrated in Equations 18–24, which subsequently react with solute.

Selective generation of radicals by pulse radiolysis:

$$\mathrm{H_2O} \rightarrow e^-_{\mathrm{aq}}, \mathrm{H^\bullet}, \mathrm{HO^\bullet}, \mathrm{HO_2^\bullet}, \mathrm{H_2O_2}, \mathrm{H_3O^\bullet} \tag{18}$$

$$e^-_{\mathrm{eq}} + \mathrm{N_2O} + \mathrm{H_2O} \rightarrow \mathrm{N_2} + \mathrm{HO^\bullet} + \mathrm{HO^-} \tag{19}$$

$$\mathrm{HO^\bullet} + (\mathrm{CH_3})_3\mathrm{COH} \rightarrow \mathrm{H_2O} + {}^\bullet\mathrm{CH_2C(CH_3)_2OH} \tag{20}$$

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{-\bullet} \tag{21}$$

$$HO^\bullet + CO_3^{2-} \rightarrow CO_3^{-\bullet} + HO^- \tag{22}$$

$$HO^\bullet + N_3^- \rightarrow N_3^\bullet + HO^- \tag{23}$$

$$HO^\bullet + CH(Me_2)OH \rightarrow {}^\bullet C(Me_2)OH + HO^- \tag{24}$$

Although a number of radicals can be produced from water (eq. 18), the prime species are the hydroxyl radical and the solvated electron. The hydroxyl radical is selectively produced by saturating the solution with nitrous oxide, to eliminate the solvated electron (eq. 19). Alternatively, the solvated electron is selectively generated by de-activating hydroxyl radicals with *t*-butanol (eq. 20).

The hydroxyl radical is a powerful one-electron oxidant (redox potential 2.75 V, NHE) and its reactions can be classified into four different types: (a) addition to aromatic or unsaturated compounds to form a hydroxyl-adduct free radical, (b) hydrogen atom abstraction to form water and a free radical, (c) electron-transfer oxidations, and (d) disproportionation reaction. Other radicals can be produced from the primary radicals and these can participate in more selective reactions. For example, the azidyl radical (redox potential 1.6V, NHE) is generated from reaction of hydroxyl radicals with azide (eq. 23) and this is employed for one-electron oxidation reactions. The carbonate radical anion (redox potential 1.6V, NHE) can be used to check one-electron oxidation reactions (eq. 22). The sulfate radical anion (eq. 21) is also a selective and powerful one-electron oxidant with a redox potential of 3.1 V (NHE), and can be used under conditions where radical generation from azide is difficult, eg low pH's or for more intractible substrates. Similarly, reduction reactions can be carried out with secondary alcohol radicals, eg, isopropyl alcohol radicals (eq. 24), to confirm reaction mechanisms.

*One-Electron Oxidation Reactions of Dyes.* *Formation and Decay of Dye Radicals.* The common anion form of arylazonaphthol dyes ($D^-$) reacts with the azidyl radical by electron-transfer to yield the dye radical $D^{\cdot}$

$$N_3^\bullet + D^- \rightarrow N_3^- + D^\bullet \tag{25}$$

Interestingly, despite its short lifetime, the spectrum of the dye radical spectrum, resulting from the one-electron oxidation of the common anion, was recorded for the first time (51). The spectrum of $D^\bullet$ is shifted even more towards lower wavelengths than the common anion, suggesting that it exists predominantly in the azo tautomeric form with the radical being primarily oxygen centred. The rate and extent of the reaction was unaffected by the oxygen concentration in solution consistent with the radical being hetero-atom centered.

Plots of the rate of dye radical decay against radical concentration were linear. This demonstrates that the dye radical decays by a second-order process resulting in dye decolorization:

$$2D^\bullet \rightarrow D^- + D^+ \tag{26}$$

$$D^+ \rightarrow \text{Bleached Dye} \tag{27}$$

The disproportionation or termination rate constant, $k_t$, of the Dye was calculated using the expression:

$$2\,k_t = (\tau_{1/2})^{-1}/[D^{\bullet}] \tag{28}$$

and found to equal $2.5 \times 10^9\ \mathrm{M}^{-1}\mathrm{cm}^{-1}$.

*Mechanism of Electron-Transfer Mediated Dye Bleaching.* The overall mechanism of dye decolorization involves two consecutive one-electron transfer steps, the initial formation of the dye radical followed by disproportionation (Fig. 11).

Removal of the second electron upon disproportionation results in formation of a carbenium ion at position 1 of the naphthol ring. Further dye degradation results from subsequent hydrolysis of the carbenium ion to yield the corresponding naphthoquinone and diazene species, which is subject to further oxidation as illustrated earlier (39,40).

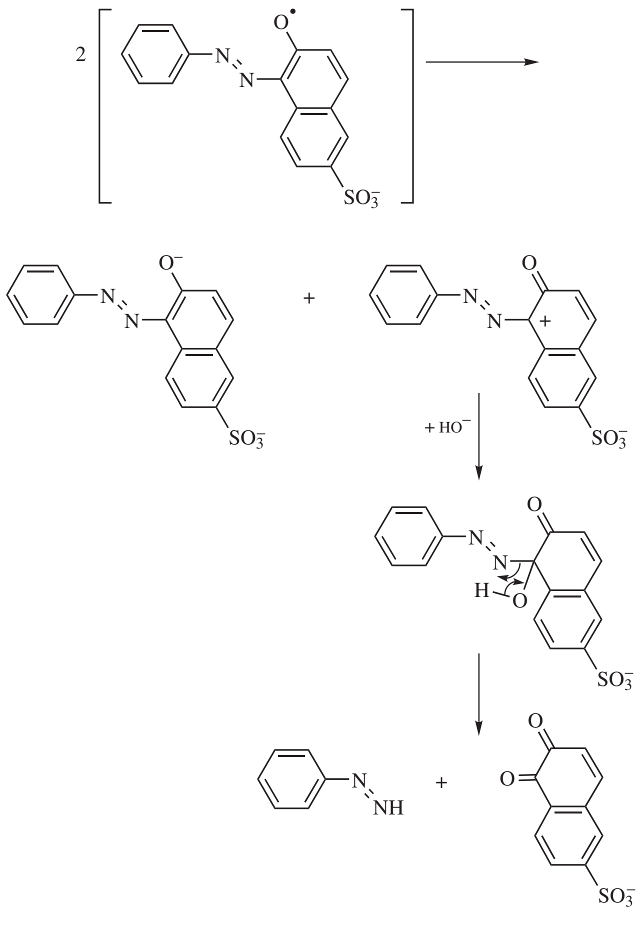


**Fig. 11.** Formation of dye radical followed by disproportionation.

If the reaction takes place under conditions where the common anion concentration is insignificant, then electron transfer reaction occurs (50) with the hydrazone tautomeric form, albeit at lower rate ($1.1 \times 10^8$ vs $5 \times 10^9$ $M^{-1}cm^{-1}$), and with initial electron transfer oxidation at the hydrazone nitrogen atom.

The so-formed radical cation has a $pK_a \sim 5$, so at pH $>5$ will undergo prototropic equilibrium to form the dye radical, which subsequently disproportionates as in Fig. 11.

*Significance.* Typical one-electron oxidants- including peroxidase enzymes, which perform two consecutive one-electron substrate oxidation steps have, or generate intermediates with, redox potentials of 0.8–0.9 V. Consequently, they would be able to oxidize the dye common anion (0.7 V) but unlikely to allow direct oxidation of the azo (1.4 V) or hydrazone (1.0 V) dye tautomers. The active dye species for peroxidases, metal catalysts and organic oxidants is therefore likely to be the dye common anion, with disproportionation of the dye radical giving rise to the bleached species. Indeed, the reactivity of dye form to oxidation follows the series:

$$\text{common anion} > \text{hydrazone} > \text{azo} >$$

Much interest has been focused recently on the potential use or peroxidases in detergents, particularly to oxidize fugitive dyes, thereby preventing their transfer onto other garments in the domestic wash (52). Thus, mechanism of dye degradation by peroxidase enzymes is briefly discussed.

The active site in peroxidases where catalysis occurs, is normally a ferric heme, ie, iron (III) porphyrin, in which a fifth ligand is an imidazole of the protein (Fig. 12). It is generally believed that the mechanism of action follows the scheme illustrated in Figure 13.

Compound I is a powerful oxidizing agent, formed by the double-oxidation of the heme group. It is believed to contain iron in the Fe(IV) state and the second oxidation occurs on the porphyrin ring. It reacts with substrates, S, to form Compound II, a result of one electron reduction of the porphyrin ring and is usually accompanied by proton transfer from substrate. The peroxidatic reaction is completed by reduction of Compound II by substrate, to regenerate the peroxidase enzyme.

Thus, dye bleaching via one-electron oxidation of the common dye anion to a labile radical is considered to represent a hitherto unrecognized and very

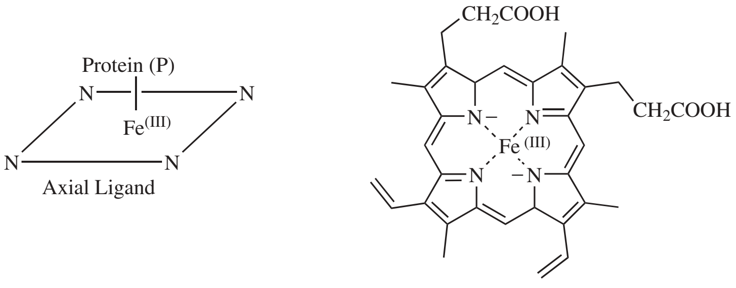


**Fig. 12.** Active site of peroxidases.

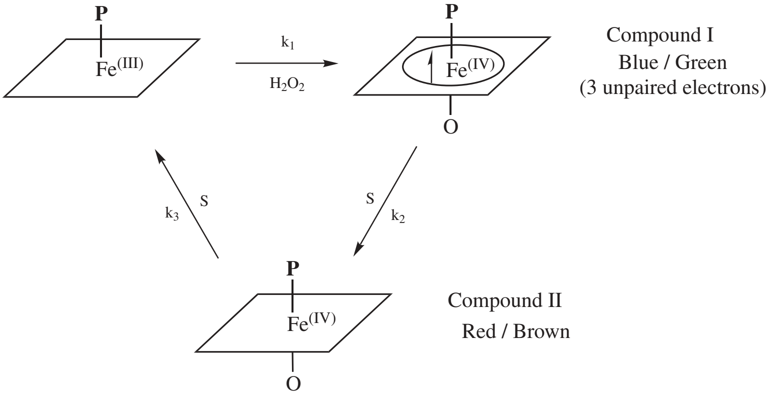


**Fig. 13.** Mechanism of action of peroxidases.

significant dye degradation pathway. Indeed, the bimolecular disproportionation reaction of dye radicals generated by one-electron oxidation of the common anion represents a novel and generic route for bleaching of azo dyes. Thus both the *electron transfer and oxygen atom* transfer oxidation reactions are controlled by the common anion thus both will increase with decrease in dye p$K_a$. One electron oxidation of dyes containing reducing groups, eg, $NH_2$, is not dependent upon the dye p$K_a$ but will decrease upon protonation of the reducing group, normally in acid media.

*Reduction of Azo Dyes.* Rate constants for the reaction of the solvated electron with the hydrazone tautomeric forms arylazonaphthol dyes are diffusion controlled (50), similar to those for simple azo dyes, eg, substituted azobenzenes (53). Reaction of the isopropyl alcohol radical with the parent dye is an order of magnitude lower but generates the same intermediates.

The reaction mechanism is illustrated in Fig. 14.

The solvated electron reacts at the nitrogen atom adjacent to the naphthol moiety yielding the dye anion. This is protonated instantly by water leading to formation of the hydrazyl radical. In turn, this decays (lifetime $< 200$ μs) bimolecularly by disproportionation to the hydrazide. This further degrades via disproportionation over longer timescales to produce amines; as outlined earlier in the reduction of simple azo dyes, eg, substituted azobenzenes.

Like oxidation reactions- both oxygen atom and electron transfer the reduction reaction depends strongly upon the dye tautomeric form. In particular, the rate reduces upon formation of the common anion, ie the reduction reaction is favoured by increase in dye p$K_a$. Indeed, the reactivity of dye form to reduction follows the series:

$$\text{azonium ion} > \text{hydrazone} > \text{azo} > \text{common anion}$$

*Reactions of Hydroxyl Radicals.* Hydroxyl radicals generally react with arylazonaphthol dyes over a wide range of pH by addition reaction, H-atom

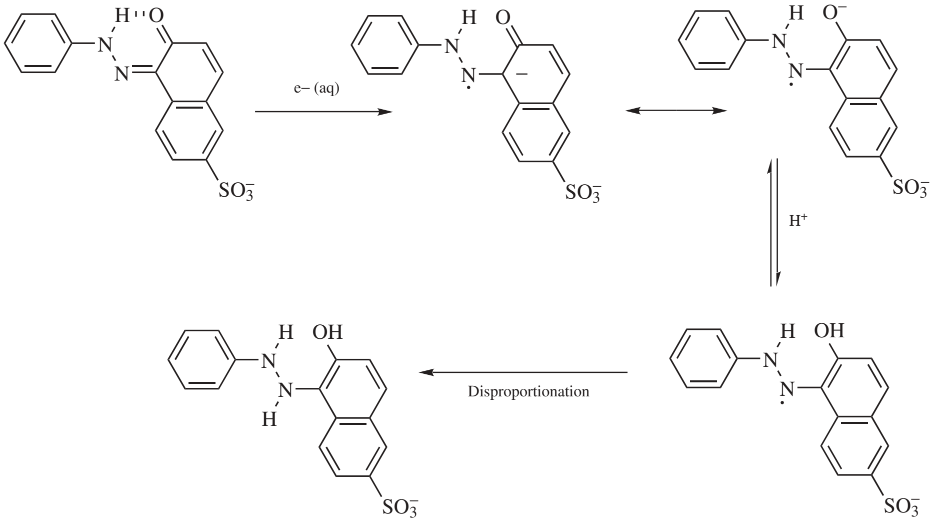


**Fig. 14.** Reduction of arylazonaphthol dyes at pH 7.

abstraction or electron transfer reactions. Insertion and electron transfer reactions tend to be diffusion controlled; H-atom abstraction from the β-nitrogen of the hydrazone tautomeric form would be expected to be 1–2 orders lower. Rates are not influenced by substituent, and addition reaction occurs at the benzene or naphthol ring, the latter being favored as it is a lower energy system and because the radical product is insensitive to oxygen. The reaction intermediate has a short lifetime ($<200\ \mu s$) as it is efficiently bleached by bimolecular dimerisation, ie, reaction stoichiometry is 1 hydroxyl radical per dye.

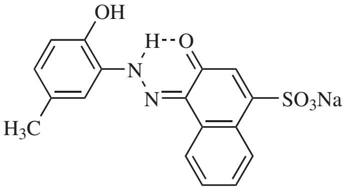
Bleaching of dyes by hydroxyl radicals represents the most efficient route studied to date. Its reactions are indiscriminate, bleaching all common dye tautomeric forms, ie reaction with *azo, hydrazone or common anion* form of dyes occurs with equal facility. However, insertion reactions of $O^{-\bullet}$ formed by dissociation of hydroxyl radicals:

$$OH^{\bullet} \Leftrightarrow O^{-\bullet} + H^{+} \tag{29}$$

tends to occur at reduced rates.

**4.5. Dye Degradation by Metal Catalysis – High Oxidation State Species.** This section is concerned with the catalyzed oxidation by addition of metal ions or complexes, where high oxidation state metal species are usually implicated as reactive species. In direct parallel to oxygen-atom transfer mechanisms by peracids, only a tiny fraction of the metal catalyst is actively involved in promoting dye oxidation (54,55). This is exhibited in unusual but interesting kinetic features, which provides an elegant and unique insight into mechanisms of oxidation that is normally difficult to obtain *via* other methods.

*Manganese-Catalysed Dye Oxidation.* Addition of Mn(II) ions to Calmagite (**33**) in alkaline media results in rapid catalysed bleaching of the dye, in presence of hydrogen peroxide or peroxosulphate (54).



(**33**)

The decomposition profiles for the Mn(II)-catalyzed peroxide or monopersulfate oxidation of Calmagite are unique; as the reaction proceeds and the dye concentration decreases, the reaction accelerates. Furthermore, the initial reaction rate is slower when the initial dye concentration is increased. Calmagite is a good ligand for $Mn^{2+}$, even in alkaline media, and the unusual kinetic profiles can be understood in terms of the unusually low redox potential of Calmagite (~0.5 V, NHE), and the formation of two discrete complexes that can each be detected by uv-visible spectroscopy upon titration with Mn(II) ions:

$$[Mn] + [D] \overset{k_1}{\rightleftharpoons} [MnD] \tag{30}$$

$$[MnD] + [D] \overset{k_2}{\rightleftharpoons} [MnD_2] \tag{31}$$

It is shown that MnD is the active species and that the order in $[D]$ is $-1$. As MnD is the catalytically active species whose concentration increases as dye is degraded, ie, as as $MnD_2$ is converted to MnD according to equilibrium expressions, then this provides the rationale for the order of $-1$ in $[D]$.

The mechanism of manganese- catalyzed oxidation of Calmagite is attributable to a one-electron transfer process whereby bound Mn(II) becomes oxidized to Mn(III) which, in turn, induces direct oxidation of Calmagite to which it is bound *via* one-electron oxidation.

*Copper-Catalyzed Dye Oxidation.* Addition of $Cu^{2+}$ ions to Calmagite also produces unusual kinetic profiles for dye oxidation (55), normally characterized by an induction period. In this case, uv-vis studies indicate that $Cu^{2+}$ forms a 1:1 complex with Calmagite of high stability constant, ($\log K = 21$). In contrast to manganese catalysis, binding of $Cu^{2+}$ actually protects the dye against oxidation and catalysis is observed only when $[Cu^{2+}] > [D]$, or when sufficient $Cu^{2+}$is released by oxidation of CuD, or with dyes that exhibit little binding. Oxidation of CuD occurs more readily with peroxosulfate than with peroxide, so that catalysis is observed in the former case only.

The reactions leading to Calmagite decolorization are:

Uncomplexed dye

$$\mathrm{D} + \mathrm{HSO}_5^- \rightarrow \text{products} \tag{32}$$

Complexed dye

$$\mathrm{CuD} + \mathrm{SO}_5^{2-} \rightarrow \text{products} + \mathrm{Cu(OH)}_2 \tag{33}$$

Catalyzed

$$\mathrm{CuD} + \mathrm{SO}_5^{2-}/\mathrm{HSO}_5^{-} \xrightarrow{\mathrm{Cu(OH)}_2} \text{products} \tag{34}$$

These reactions can be used to predict experimentally determined kinetic profiles and to compute changes in various solution species as the reaction proceeds.

The speciation profiles clearly indicate that the active catalyst is $\mathrm{Cu(OH)}_2$ and that the Cu/Calmagite complex is catalytically inert. Overall, the results are consistent with a mechanism in which a high surface area intermediate, formed during the precipitation of $\mathrm{Cu(OH)}_2$, is the active catalyst. This appears to have a high affinity for the reactants and it functions by increasing the effective reactant concentrations through rapid adsorption upon its surface.

*Iron Porphyrin-Catalyzed Dye Oxidation.* The oxidation of model dyes by peracids in solution catalyzed by iron porphyrins that are sterically hindered to prevent dimerization demonstrate a rich variety of chemistry in which the catalyst can function by a number of different mechanisms, depending upon the conditions (56,57). The basic mechanism, which involves formation of two high oxidation states of the porphyrin is now well understood. Initially, the Fe(III) porphyrin, Fe(III)P, is oxidized by peracids by a concerted two electron transfer to form a high oxidation state oxoiron(IV) porphyrin cation radical, $\mathrm{OFe(IV)P}^{+\bullet}$, which is a powerful oxidant (Fig. 15). This can undergo a rapid comproportionation reaction with the original porphyrin to form an Fe(IV) species, OFe(IV)P, [(**34**) and Fig. 15] a less powerful oxidant. The latter can also be formed by reaction of the oxo-iron(IV) porphyrin cation radical with peracid. Both these high oxidation species are capable of bringing about dye destruction.

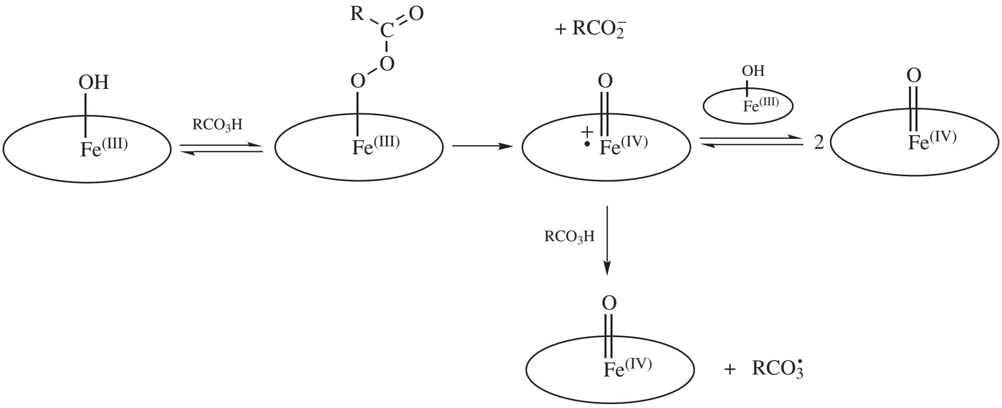
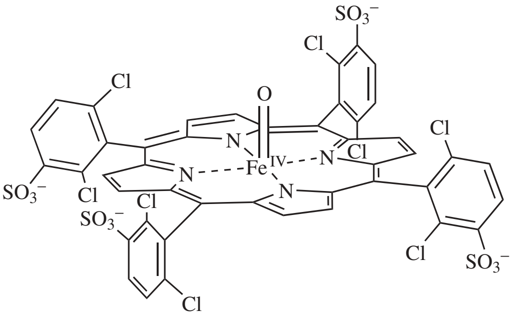


**Fig. 15.** Mechanism of formation of the two oxo-iron (IV) species, $\mathrm{O{=}Fe(IV)P}^{+\bullet}$ and $\mathrm{O{=}Fe(IV)P}$.



Both the O = Fe(IV)P species and dye and dye exhibit acid-base equilibria, the former having a p$K_a$ of 7.1 (Fig. 16) and the dye at 10.8

The reaction depends on pH, demonstrating that certain species of the reactants are more reactive than others. The pH dependence can be explained primarily by electron transfer reaction between dye common anion and OFe(IV)P(OH) in strongly basic solution, and hydrogen atom abstraction by OFe(IV)P($OH_2$) from the *azo* tautomer of the dye at neutral pH.

Consistent with this view, the redox potential of the OFe(IV)P species is 1.29 V (NHE), ie, can oxidize both anionic (~0.7 V) and undissociated form of the dye (~1 V).

Under catalytic conditions, the more reactive OFe(IV)$P^{+\bullet}$ species participates in dye oxidation and has been demonstrated to oxidize dyes by an oxygen-atom transfer mechanism, *via* initial insertion of a hydroxyl group at the imine carbon of the dye common anion in strongly alkaline media or formation of an azoxy compound at lower pHs.

Evidently, iron porphyrins are versatile catalysts which can oxidize dyes by a variety of mechanisms depending upon the conditions.

**4.6. Photofading.** The color of dyes arises from absorption of light in the visible region, and is generally the result of n-$\pi^*$ and $\pi$-$\pi^*$ electronic transitions. However, the very process of absorption of light raises the molecule to an electronically excited state which tends to be more polarized, ie, has greater charge separation, and is hence more reactive than the ground state molecule. At the outset, examination of the literature (42) shows that photochemistry of dyes may be extremely complex, may contain impurities or exist in various states of aggregation, or contain certain substituents that are photoactive in their own right. Nevertheless, this section outlines the general principles with selected

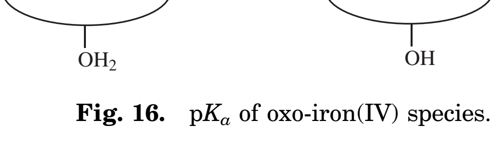


**Fig. 16.** p$K_a$ of oxo-iron(IV) species.

illustrations, the intention is to accommodate the diverse behavioural patterns and present to the reader a simpler, yet accurate, perspective.

*Photofading via Excited Singlet States.* Normally, singlet excited states, $HD^*$, produced when a molecule absorbs a photon of light are too short-lived to participate in conventional photochemical reactions. However, *photofading* is a relatively inefficient process, with typical quantum yields of the order $10^{-5}$, ie, only 1 in 100,000 photons absorbed leads to photodegradation. So, even where the higher excited singlet state lifetimes are exceedingly short ($10^{-12}$s), there is still a finite probability that photofading will occur for reactions with high intrinsic rates ($k_1 > 10^6\ s^{-1}$):

$$\mathrm{HD} \rightarrow \mathrm{HD}^\bullet \rightarrow \text{Decomposition} \tag{35}$$

The energy level of an excited singlet state is higher than that of the respective triplet state, and so has a higher energy content, making it potentially more reactive. On the other hand, the triplet state has a longer lifetime, so, in general, it has more chance of reacting. Textile dyes may react in the excited singlet state despite short lifetimes, simply because they are in direct contact with reactive groups on the fabric. However, the probability that the dye reacts with molecular oxygen is higher for the triplet state, since oxygen is required to diffuse into the immediate neighborhood of the dye.

*Photooxidation via Singlet Oxygen.* If the dye is excited to a triplet state, it may undergo triplet-triplet annihilation with oxygen to produce singlet oxygen (eq. 36) which may initiate dye destruction (eq. 37):

$$^3\mathrm{HD}^\bullet + {}^3\mathrm{O}_2 \rightarrow \mathrm{HD} + {}^1\mathrm{O}_2 \tag{36}$$

$$^1\mathrm{O}_2 + \mathrm{HD} \rightarrow \text{Decomposition} \tag{37}$$

Most dyes can be degraded by singlet oxygen and this degradation reaction tends to predominate in the presence of singlet oxygen sensitizers. Such sensitizers transfer their energy from the lowest excited triplet states to the acceptor (molecular oxygen). The acceptor is raised to an excited state and the excited donor molecule reverts to the ground state.

The principle of photosensitization is well known and the underlying mechanism, the *ene* reaction, was elucidated by Griffiths (58). In the presence of the singlet oxygen sensitizer methylene blue in alcoholic solvents, the photochemical pathway was found to proceed via singlet oxygen attack on the hydrazone form of the dye via an unsaturated azo hydroperoxide intermediate as shown in Fig. 17.

This represents a so-called *Type 2* photooxidation process, since the primary reaction products do not involve radicals.

Other dyes that are readily degraded by singlet oxygen are polymethine and arylmethine dyes, indigo and sulfur dyes. Despite the preponderance of evidence that singlet oxygen can be generated from dyes and that many dye types can quench singlet oxygen either physically ($k_2{\sim}10^{7-8}\ M^{-1}s^{-1}$) or chemically ($k_2{\sim}10^{4-5}\ M^{-1}s^{-1}$), eg, phthalocyanines, it does not necessarily follow that reaction with singlet oxygen is a major decomposition pathway for dyes in solution or, particularly, when bound to textiles.

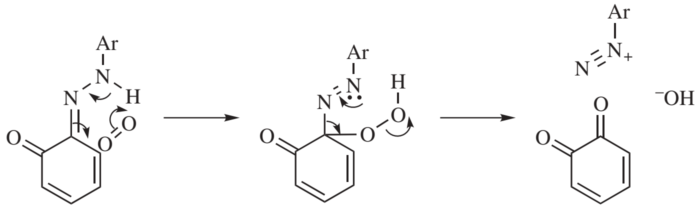


**Fig. 17.** Mechanism of oxidation of azo dyes by singlet oxygen.

*Photooxidation by Superoxide.* Oxygen may also participate in photooxidation of dyes via electron-transfer reactions with electronically excited states to generate superoxide (eq. 38). Visible light is capable of facilitating this transformation and photo-excited singlet or triplet states may be involved. Decolourization of dye may result from spontaneous decomposition of $HD^{+\bullet}$ or from subsequent reaction of superoxide with dye (eq. 39).

$$HD^{\bullet} + O_2 \rightarrow HD^{+\bullet} + O_2^{-\bullet} \qquad (38)$$

$$O_2^{-\bullet} + HD \rightarrow \text{Decomposition} \qquad (39)$$

*Photoreductive Pathways.* Photoreductive processes generally involve radicals but high energy light (uv or near uv) is required to facilitate their formation via bond cleavage. For example, the excited state of dyes, $HD^{\bullet}$, are more reactive than the ground state and may photoionize upon uv-irradiation:

$$HD^{\bullet} \Rightarrow HD^{+\bullet} + e^{-} \qquad (40)$$

and the ejected electron may add to another dye molecule:

$$HD + e^{-} \Rightarrow HD^{-\bullet} \qquad (41)$$

Other reaction pathways are illustrated in equation 42–44. These involve hydrogen atom abstraction by $HD^{\bullet}$ from RH of neighboring molecules to form $H_2D^{\bullet}$ and $R^{\bullet}$ (eq. 42). In turn, subsequent reactions 43–45 may follow. Both $R^{\bullet}$ and peroxy radicals, $RO_2{}^{\bullet}$, can cause dye degradation (eq. 45):

$$HD^{\bullet} + RH \rightarrow H_2D^{\bullet} + R^{\bullet} \qquad (42)$$

$$H_2D^{\bullet} \rightarrow \text{Decomposition} \qquad (43)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad (44)$$

$$R^{\bullet}/RO_2^{\bullet} + HD \rightarrow \text{Decomposition} \qquad (45)$$

$$H_2D^{\bullet} + O_2 \rightarrow HD + O_2^{-\bullet} + H^{+} \qquad (46)$$

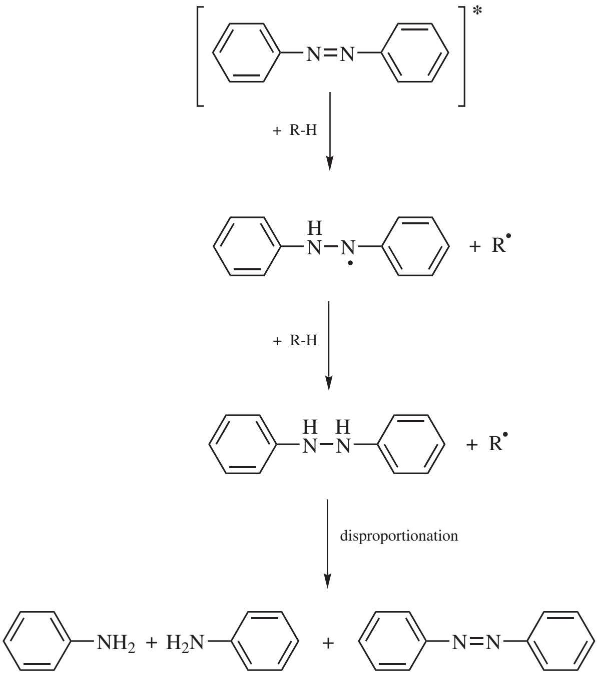


**Fig. 18.** Direct photoreduction of azobenzene.

The radical, $H_2D^\bullet$, formed in (eq. 42) may also react with RH to generate $H_3D$ and $R^\bullet$ as illustrated in Fig. 18.

The reactions 38,39,42,45 collectively represent so-called *Type 1* photoredox pathway, since the primary reaction products are radicals.

If the process shown in (eq. 46) occurs, then the dye is acting as a sensitiser for *Type 1* photooxidations, ie, it is not consumed in the overall process but helps to initiate and propagate free-radical processes involving the substrate (eg, phototendering). However, although in such cases the dye may not be consumed directly in these photochemical processes, the high build up of peroxides in the substrate, for example via eq. 47.

$$O_2^{-\bullet} + HO_2^\bullet + H^+ \rightarrow H_2O_2 + O_2 \tag{47}$$

which can occur at rates, $k_2 \sim 10^{8-9}\ M^{-1}s^{-1}$, can lead to indirect and irreversible oxidative bleaching of the dye. The type of fading illustrated in (eq. 42–46) is commonly observed with quinone dyes, which have long-lived triplet states. Thus, whereas these dyes readily undergo photoreduction, their long term degradation products result from oxidative processes.

Radicals can also be generated by bond dissociation upon irradiation by light in the uv region:

$$HD^\bullet \rightarrow R_1^\bullet + R_2^\bullet \tag{48}$$

where $R_1^{\bullet}$ and $R_2^{\bullet}$ represent radicals generated from the dye itself. Subsequent photo-oxidative degradation proceeds according to reactions 44 and 45 in an overall photoreductive degradation scheme.

Generally, although few mechanistic details have been elucidated, the mechanism of direct photoreductive cleavage of azo dyes appears to be generally accepted. It is believed that electron-addition to azo dyes is accompanied by the simultaneous uptake of a proton, initially to form hydrazyl intermediates, then the corresponding hydrazo compound. These, in turn, can be thermally unstable under certain conditions with respect to disproportionation, yielding aromatic amines as reaction products.

A typical scheme which shows the direct photoreduction of azobenzene is illustrated in Fig. 18.

The initial step involves abstraction of a hydrogen atom from the solvent by the photoexcited state of the azo compound. Hydrazobenzene can be detected as intermediate under certain circumstances.

*Influence of Substrate.* The substrate to which the dye is bound can also undergo excitation and/or participate in electron transfer, hydrogen abstraction or bond dissociation mechanisms. A common example is excitation of substrates containing carbonyl groups, which can mediate via hydrogen atom abstraction from other functional groups of the substrate (eq. 50) or even the dyes themselves (eq. 51):

$$R_2C{=}O \overset{uv}{\rightarrow} [R_2C{=}O^*]^1 \rightarrow [R_2C{=}O^*]^3 \tag{49}$$

$$[R_2C{=}O^*]^3 + R-H \rightarrow R_2C^{\bullet}{-}OH + R^{\bullet} \tag{50}$$

$$[R_2C{=}O^*]^3 + HD \rightarrow R_2C^{\bullet}{-}OH + D^{\bullet} \tag{51}$$

Furthermore, radicals like $R_2C^{\bullet}$-OH are extremely good one-electron reductants (oxidation potential $-1.3$V in water, $-0.7$ V in acetonitrile, typical rates, $k_2 \sim 10^{7-9}\ M^{-1}s^{-1}$), and this schematically illustrated for dyes in eq. 52.

$$R_2C^{\bullet}{-}OH + HD \rightarrow R_2C{=}O + HD^{-\bullet} + H^+ \tag{52}$$

*Dye-Induced Phototendering of Textiles and Photofading.* Many yellow, orange and red vat dyes (anthraquinone dyes) are known to promote damage to cellulose (39,40). These absorb disproportionately more in the energy intensive part of the visible spectrum but are more resistant to oxidation than corresponding blue or black dyes. Some sulfur and basic dyes are also known to exhibit phototendering. The mechanism of action of the dye-sensitized oxidative degradation of cellulose has become much clearer as a result of work done in the 1970s. It appears that the initial step in cellulose degradation is the removal of a hydrogen atom (or electron) by the excited dye molecule. Typical events are illustrated in the sequence of reactions 42–46 explained previously.

Although yellow dyes may be expected to be more prone to photofading due to absorption in the energy intensive part of the visible spectrum, in fact, the ease of photodegradation of azo dyes tends to follow the order:

$$\text{blues} > \text{reds} > \text{yellows}$$

ie, in line with the order of decreasing conjugation, hence chemical reactivity. For similar reasons, yellow pyrazolone and pyridone dyes which adopt the more conjugated hydrazone form are more susceptible to (photo)oxidation than yellow dyes that exist solely in the azo form. Some metal complexed azo dyes adopt an intermediate position. Extending this argument, the general susceptibility of dyes to oxidation follows the order:

polyenes $\sim$ poly-and aryl-methines $>$ azos $>$ phthalocyanines $>$ anthraquinones

with the first two members of the series being readily oxidized by singlet oxygen or hydrogen peroxide.

## 5. Dyeing Classes: Structure, Application, Uses

Of all classes of dyestuffs, azo dyes have attained the widest range of usage because variations in chemical structure are readily synthesized and methods of application are generally not complex. There are azo dyes for dyeing all natural substrates such as cotton, paper, silk, leather, and wool; and there are azo dyes for synthetics such as polyamides, polyesters, acrylics, polyolefins, viscose rayon, and cellulose acetate; for the coloring of paints, varnishes, plastics, printing inks, rubber, foods, drugs, and cosmetics; for staining polished and absorbed surfaces; and for use in diazo printing and color photography. The shades of azo dyes cover the whole spectrum.

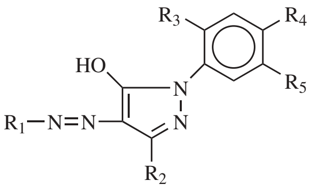
### 5.1. Acid Dyes.

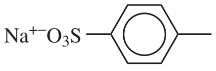
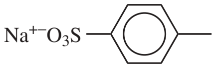
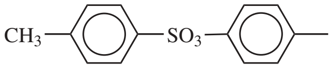
Commercial acid dyes contain one or more sulfonate groups, thereby providing solubility in aqueous media. These dyes are applied in the presence of organic or mineral acids (pH 2–6). Such acids protonate any available cationic sites on the fiber, thereby making possible bonding between the fiber and the anionic dye molecule. Wool, an animal fiber, is an amphoteric colloid, possessing both basic and acidic properties because of the amino and carboxylic groups of the protein structure. In order to dye such a system, coulombic interactions between the dye molecule and the fiber must take place; ie, $H_3N^+$-wool-$COO^-$; + $H^+ \longrightarrow H_3N^+$-wool-COOH. The term acid dye is applied to those that are capable of such interactions. Acid dyes themselves are not generally acids (ie, dye-$SO_3H$) but are sulfonate salts (dye-$SO_3Na$) of strong sulfonic acid groups.

There are three general classifications of acid dyes depending on their method of application: acid dyes that dye directly from the dyebath, mordant dyes that are capable of forming metallic lakes on the fiber when aftertreated with metallic salts, and premetallized dyes.

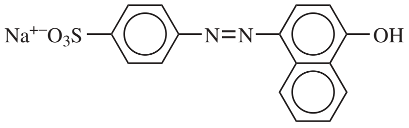
Acid Yellow 23 (**35**), commonly known as Tartrazine was first discovered in 1884 and is made by coupling equimolar quantities of diazotized sulfanilic acid to 3-carboxy-1-(*p*-sulfophenyl)-5-pyrazolone. Other monoazopyrazolone dyes of commercial importance include Acid Yellow 17 (**36**) (sulfanilic acid $\longrightarrow$ 1-(2,5-dichloro-4-sulfophenyl)-3-methyl-5-pyrazolone and Acid Yellow 40 [6372-96-9] (**37**) (CI 18950) (*p*−aminophenol$\longrightarrow$ 1-(4-chloro-2-sulfophenyl)-3-methyl-5-

pyrazolone) followed by esterification of the phenolic hydroxy group with *p*-toluenesulfonyl chloride.

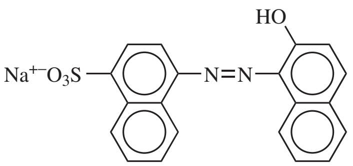


| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| (**35**) |  | $COO^-Na^+$ | H | $SO_3H$ | H |
| (**36**) |  | $CH_3$ | Cl | $SO_3^-Na^+$ | Cl |
| (**37**) |  | $CH_3$ | $SO_3^-Na^+$ | Cl | H |

With Orange I [574-69-6] (**34**) (CI Acid Orange 20; CI 14600) the naphthalene moiety was introduced to azo chemistry. Basacid Red 340 [1658-56-6] (**37**) (CI Acid Red 88; CI 15620) the first red azo dye of technical value was discovered by BASF in 1876. Its previous name was Fast Red AV and it is still produced in large amounts in the United States because of its low cost and good dyeing and fastness properties. This dye became the prototype of a large number of red azo dyes that were developed simultaneously with the introduction of new derivatives of naphthalene.

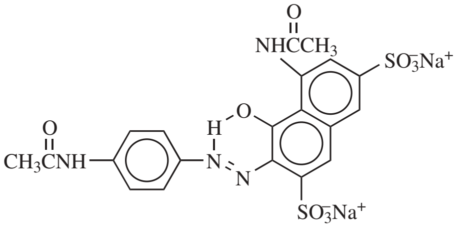


(**38**)



(**39**)

In textile dyes, it is important that hydroxyl and amino groups be ortho to azo, carboxyl, or sterically bulky groups. In dyes such as Anthosin Orange 35 (**21**), Chrysoidine (**22**), and Basacid Red 340 (**39**) hydrogen bonding shifts the acid base equilibrium to pH regions ($pH < 2$ or $>11$) outside those ordinarily employed in textile processing. In Acid Orange 20 (**38**) hydroxyl group dissociation leads to tint changes in alkaline washing tests. If coupling in the ortho position to a hydroxyl or amino group cannot be attained (eg, in the case of unsubstituted phenol), these groups must be alkylated, esterified, or acylated afterward. Phenolic hydroxyl groups can be converted into esters by *p*-toluenesulfonyl chloride, as in Acid Yellow 40 (**37**). Coupling components with a second amino or hydroxyl group must also be acetylated or tosylated to get dyes of good alkaline and acid fastness. An important example is Amido Naphthol Red 6B [4321-69-1] (**40**) (CI Acid Violet 7; CI 18055) from acetyl H-acid. The corresponding compound with a free amino group is of no technical value.



(**40**)

Instead of acetyl groups, other acyl and aroyl groups can be utilized which, conveniently and characteristically, change the dyeing properties (Fig. 19). To get good leveling properties, these dyes require a dyeing pH of 4–6.5. Longer alkyl chains in the diazo component also increase the wash fastness. This effect is caused by hydrophobic interactions (59). Other commercially important azo acid dyes, are listed in Tables 5 and 6.

Of these dyes, Acid Yellow 151 (**41**) still has the greatest market among the yellows. It is produced by coupling diazotized 2-amino-1-phenol-4-sulfonamide to

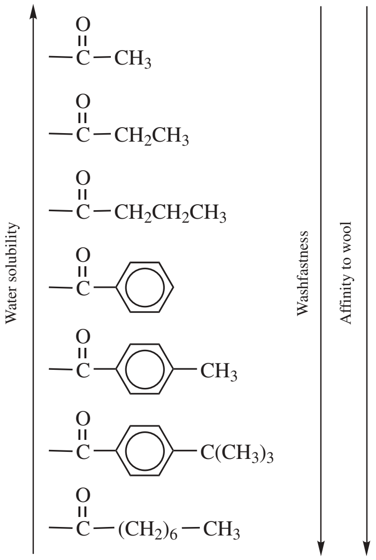


**Fig. 19.** Dyeing characteristics as affected by various blocking groups. Water solubility decreases; washfastness and affinity increase.

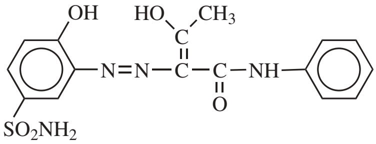
Table 5. **Yellow and Orange Commercial Azo Acid Dyes**

| CI name | Structure number | CAS Registry number | CI number | Chemical type |
|---|---|---|---|---|
| Acid Yellow 34 | | [6359-90-6] | 18890 | monoazo |
| Acid Yellow 36 | | [587-98-4] | 13065 | monoazo |
| Acid Yellow 49 | | [12239-15-5] | 18640 | monoazo |
| Acid Yellow 59 | | [5601-29-6] | 18690 | monoazo, metallized |
| Acid Yellow 65 | | [6408-90-8] | 14170 | monoazo |
| Acid Yellow 99 | | [10343-58-5] | 13900 | monoazo, metallized |
| Acid Yellow 135 | | [74082-21-6] | 14255 | monoazo |
| Acid Yellow 151 | (**41**) | [12715-61-6] | 13906 | monoazo, metallized |
| Acid Yellow 200 | | [6359-95-1] | 18930 | monoazo |
| Acid Orange 7 | (**21**) | [633-96-5] | 15510 | monoazo |
| Acid Orange 10 | | [1936-15-8] | 16230 | monoazo |
| Acid Orange 24 | (**42**) | [1320-07-6] | 20170 | disazo |
| Acid Orange 60 | | [12731-53-2] | 18732 | monoazo, metallized |
| Acid Orange 156 | | [68555-86-2] | 26501 | disazo |

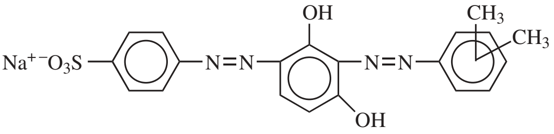
acetoacetanilide followed by metallizing with cobalt to obtain a 1:2 cobalt complex. Acid Orange 24 (**42**), which is sulfanilic acid coupled to resorcinol to which diazotized mixed xylidines have been coupled, is an unsymmetrical primary diasazo dye with a bifunctional coupling component.

Table 6. **Other Commercial Azo Acid Dyes**

| CI name | Structure number | CAS Registry number | CI number | Chemical type |
|---|---|---|---|---|
| Acid Red 4 | | [5858-39-9] | 14710 | monoazo |
| Acid Red 14 | (**56**) | [3567-69-9] | 14720 | monoazo |
| Acid Red 18 | | [2611-82-7] | 16255 | monoazo |
| Acid Red 73 | | [5413-75-2] | 27290 | disazo |
| Acid Red 85 | | [3567-65-5] | 22245 | disazo |
| Acid Red 88 | (**39**) | [1658-56-6] | 15620 | monoazo |
| Acid Red 114 | (**44**) | [6459-94-5] | 23635 | disazo |
| Acid Red 137 | | [6222-63-5] | 17755 | monoazo |
| Acid Red 151 | (**43**) | [6406-56-0] | 26900 | disazo |
| Acid Red 186 | | [52677-44-8] | 18810 | monoazo, metallized |
| Acid Red 266 | | [12217-37-7] | 17101 | monoazo |
| Acid Violet 3 | | [1681-60-3] | 16580 | monoazo |
| Acid Violet 7 | (**40**) | [4321-69-1] | 18055 | monoazo |
| Acid Violet 12 | | [6625-46-3] | 18075 | monoazo |
| Acid Blue 92 | | [3861-73-2] | 13390 | monoazo |
| Acid Blue 113 | (**45**) | [3351-05-1] | 26360 | disazo |
| Acid Blue 118 | | [6406-32-2] | 26410 | disazo |
| Acid Green 20 | (**46**) | [5850-39-5] | 20495 | disazo |
| Acid Brown 14 | (**27**) | [5850-16-8] | 20195 | disazo |
| Acid Black 1 | (**28**) | [1064-48-8] | 20470 | disazo |
| Acid Black 52 | (**47**) | [5610-64-0] | 15711 | monoazo, metallized |
| Acid Black 60 | | [12218-95-0] | 18165 | monoazo, metallized |
| Acid Black 63 | (**48**) | [32517-36-5] | 12195 | monoazo, metallized |

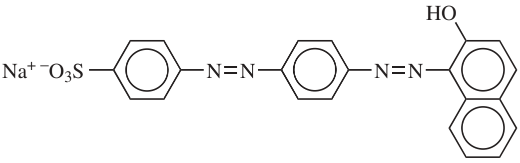


(**41**)



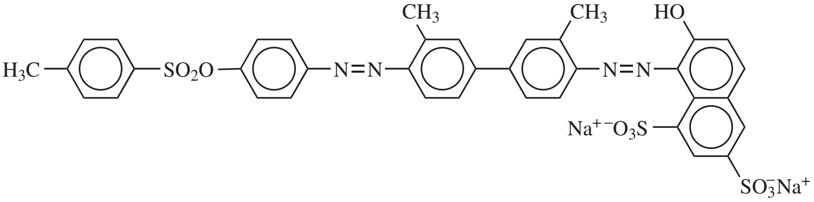
(**42**)

Economically, the most important acid red is Acid Red 151. This disazo dye (**43**) is obtained by coupling *p*(*p*-aminophenylazo)benzenesulfonic acid to 2-naphthol.



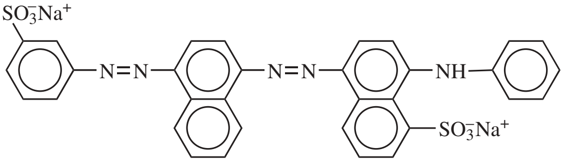
(**43**)

Other disazo dyes with good substantivity and high wet-fastness properties on polyamides are Acid Red 114 (**44**), made by coupling *o*-tolidine to phenol which is then coupled to G-acid, followed by reaction of the phenolic hydroxyl group with *p*-toluenesulfonyl chloride, and Acid Blue 113 (**44**) (metanilic acid ⟶ 1-naphthylamine ⟶ 8-anilino-1-naphthalenesulfonic acid).



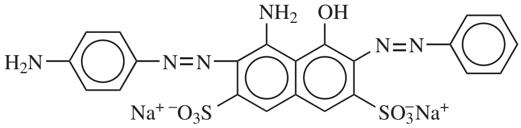
(**44**)

The largest volume acid blues are either of triphenylmethane (TPM) or anthraquinone chemical constituency (see DYES, ANTHRAQUINONE).



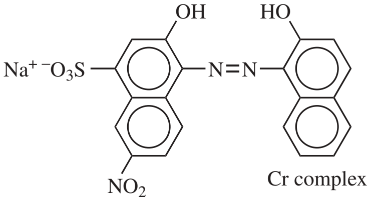
(**45**)

Among the acid colors of green, brown, and black shades, three disazo dyes are important: Acid Green 20 (**46**) (*p*-nitroaniline $\xrightarrow{\text{1-acid}}$ H-acid $\xleftarrow{\text{basic}}$ aniline, followed by reduction of the nitro group with sodium sulfide);

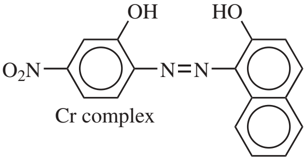


(**46**)

Acid Brown 14 (**27**) (2 mol of naphthionic acid, ie, 4-amino-1-naphthalenesulfonic acid 1 mol resorcinol); and Acid Black 1 (**28**). Two other azo acid blacks, Acid Black 52 (**47**) and Acid Black 63 (**48**) are both metallized with chromium.



(**47**)



(**48**)

Other modifications of acid wool dyes have groups which react by nucleophilic substitution of basic groups in protein fibers ($NH_2$ groups, etc). The introduction of Procion dyes by ICI in 1956 was the most important development in the field of technological azo dye chemistry. Chemically, many of the reactive dyes are prepared from the group of the anionic monoazo dyes (see DYES, REACTIVE).

**5.2. Metal Complexes of Azo Dyes.** Metal complexes of certain *o,o′*-dihydroxyazo, *o*-carboxy-*o′*-hydroxyazo, *o′*-amino-*o′*hydroxyazo, arylazosalicyclic acid, and formazan compounds are used as dyes for wool, nylon, and cotton with generally much improved washfastness and lightfastness properties when compared to their respective unmetallized precursors. Dyes that are chelated with the metal on the substrate during the dyeing process are termed metallizable or mordant dyes. Conversely, those dyes that have been metallized by the dye manufacturer prior to use by the dyer, are classified as premetallized dyes. The two important types of premetallized dyes are the 1:1 and 2:1 complexes, eg, complexes with 1:1 and 2:1 ligand-to-metal ratios, respectively.

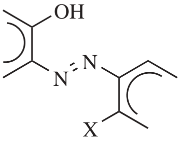
Chromium is the principal metal used with mordant dyes for wool, whereas both chromium and cobalt are used extensively in premetallized types for wool and nylon. Copper(II) is employed almost exclusively as the chelating metal ion in both metallizable and premetallized direct dyes for cotton.

An excellent review of metal complex azo dye chemistry has been provided (60). Developments in the field of metal-containing dyes have also been presented (61,62).

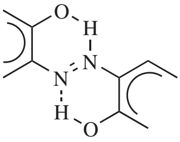
*Mordant Dyes.* Metallizable azo dyes are applied to wool by the method used for acid dyes and then treated with metal salts such as sodium chromate [7775-11-3], sodium dichromate [10588-01-9], and chromium fluoride [1488-42-5] to form the metal complex *in situ*. This treatment usually produces a bathochromic shift in shade, decreases the solubility of the coloring matter, and yields dyeings with improved fastness properties. The chromium salts can be applied to the substrate before dyeing (chrome-mordant or chrome-bottom method), together with the dye in a single bath procedure (metachrome process), or as a treatment after dyeing (afterchrome process).

Most mordant dyes are monoazo structures. The most important feature of this class of dyes is excellent fastness to light and washing. Mordant dyes are available in all shades of the spectrum with the exception of bright violets, blues, and greens. To be useful, the metal complexes must be stable, ie, must not demetallize when subjected to dyebath conditions and all aftertreatment processes, especially repeated washings. Chromium forms stable chelate rings with mordant dyes which are not affected by treatment with either weak acid or alkali (see COORDINATION COMPOUNDS).

Certain chemical configurations required to produce suitable mordant dyes are shown in the following examples of monoazo dyes. Substitution in the two positions ortho to the azo group may be illustrated by structure (**49**), in which X represents $-OH$, $-OCH_3$, $-OCH_2COOH$, $-COOH$, $-COOH_2H_5$, $-NH_2$, and similar groups. With *o,o*-dihydroxyazo dyes, hydrogen bonding involving both hydroxyl groups is possible as indicated in (**50**).



(**49**)



(**50**)

From acidity measurements it is known that one of the hydroxyl hydrogen atoms is much more strongly bound, ie, much less acidic than the other. For Eriochrome Black T [1787-61-7] (**18**b), the following equilibria apply (63), where HO-dye-OH represents the sulfonic acid salt (**18**b) as shown earlier with neither of the two OH groups neutralized.

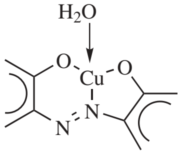
$$\text{HO}-\text{dye}-\text{OH} \rightleftharpoons \text{HO}-\text{dye}-\text{O}^- \rightleftharpoons \text{O}^- -\text{dye}-\text{O}^-$$

$$\text{wine red} \qquad \text{blue} \qquad \text{orange}$$

$$\text{p}K_{a2} = 6.3;\ \text{p}K_{a3} = 11.5$$

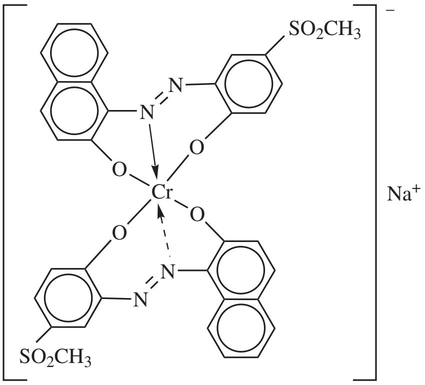
It has not been determined which hydroxyl group contains the more acidic hydrogen atom corresponding to p$K_{a2}$. Dyes of this type would behave as indicators and exhibit large color shifts with the pH range normally encountered in textile processing. Hence they are always stabilized by coordination with metal ions.

By far the most important metal containing dyes are derived from *o,o*-dihydroxyazo structures in which one of the two azo nitrogen atoms and the two hydroxyl oxygen atoms are involved in bonding with the metal ion. Thus these dyes serve as terdentate ligands. In the case of metal ions with a coordination number of four, eg, Cu(II), the fourth position is usually occupied by a solvent molecule (**51**).



(**51**)

With Cr(III) and Co(III) ions where the coordination number is six, the predominant configurations are 1:1 complexes in which solvent molecules ($H_2O$) or ions ($OH^-$;) as monodentate ligands occupy three of the positions, or a monodentate ligand and bidentate ligand such as ethylenediamine (1,2-diamino ethane) occupy three of the positions, the remaining three being occupied by the terdentate dye, and 2:1 complexes in which two terdentate dye molecules occupy all six valences. Thus, especially with metallized dyes containing chromium, it is necessary to distinguish between 1:1 and 2:1 complexes. An example of a premetallized 2:1 chromium complex azo dye is Irgalan Brown Violet DL [16073-16-8] (**52**) (CI Acid Violet 78; CI 12205).

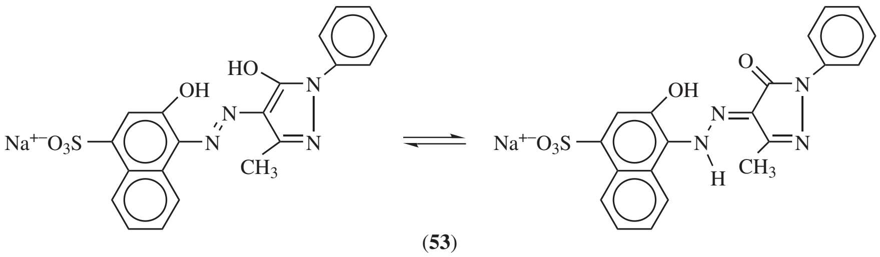


(**52**)

Using x-ray structural analyses both the meridional configuration, Drew-Pfitzner (64), and the facial configuration, Schetty-Pfeiffer (65), ligands in 2:1 chromium complexes have been confirmed. Definite coordination by one of the two azo nitrogen atoms is supported by x-ray studies, but the question of which azo nitrogen atom is involved in specific instances has not been resolved. The greater the number of annelated 5- and 6-membered chelate rings, the more stable the metal complex. Stability is also enhanced with more strongly basic ligand anions.

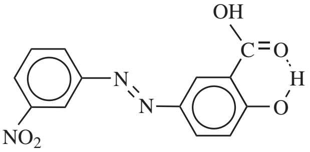
In mordant dyes, phenols, naphthols, and enolizable carbonyl compounds, such as pyrazolones, are generally the couplers. As a rule, 2:1 metal complexes are formed in the afterchroming process. A typical example of a mordant dye is Eriochrome Black T (**18**b) which is made from the important dyestuff intermediate nitro-1,2,4-acid, 4-amino-3-hydroxy-7-nitro-1-naphthalenesulfonic acid [6259-63-8]. Eriochrome Red B [3618-63-1] (**53**) (CI Mordant Red 7; CI 18760)

(1, 2, 4−acid⟶ 1-phenyl-3-methyl-5-pyrazolone) is another example. The equilibrium of the two tautomeric forms depends on the nature of the solvent.

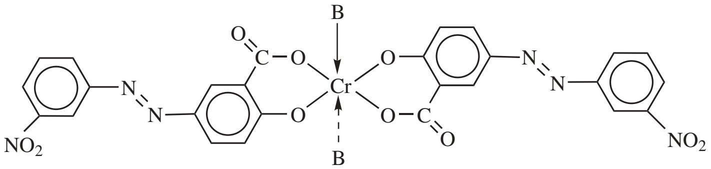


(**53**)

A hydroxyl group is situated ortho to a carboxyl group which as a bidentate ligand is terminally metallized on the fiber when aftertreated with dichromate. An example is Alizarine Yellow GG [584-42-9] (**54**) (CI Mordant Yellow 1; CI 14025). Cr(III) has a coordination number of six, and therefore normally two dye molecules of the salicylic type are chelated to the metal ion.



(**54**)



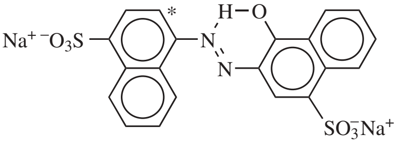
(**55**)

The other two coordination positions are available for groups of the fiber having free electron pairs, as in (**55**) where B is $-NH_2$, –NH–, or –OH.

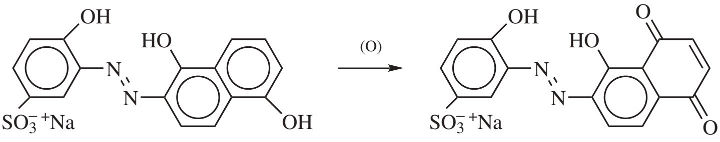
This is apparently the reason for the high washfastness of these complexes as compared to their unmetallized precursors (66). The dichromate-acid aftertreatment that is used technically oxidizes primarily cystine configurations in the wool, which converts Cr(VI) to Cr(III). Alternatively, the fiber may be pretreated with dichromate whereby essentially the same final shade is obtained, although it is not known whether the same complexes are formed.

In contrast to metal complexes of *o,o′*hydroxyazo types, these terminally metallized dyes derived from the *o*-hydroxy carboxyl structures undergo little color change on metallization and exhibit little improvement in lightfastness (67).

Certain dyes when applied by the afterchrome method are oxidized prior to metal complex formation. Examples include, Chromotrope FB [3567-69-9] (**56**) (CI Acid Red 14; CI 14720) (naphthionic acid ⟶ 1-naphthol-4-sulfonic acid) in which a hydroxyl group is introduced by oxidation at the position marked with an asterisk, after which the metal complex is formed in the usual way, and Diamond Black PV [2052-25-7] (**57**) (CI Mordant Black 9; CI 16500) in which a naphthoquinone is formed by oxidation without alteration of the original tridentate ligand.



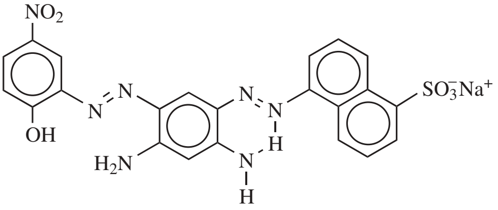
(**56**)



(**57**)

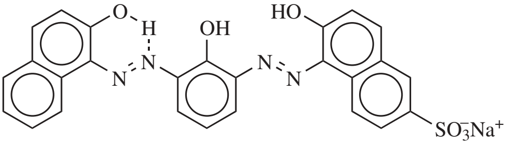
With azo dyes derived from 4,5-dihydroxy-2,7-naphthalenedisulfonic acid [148-25-4] (chromotropic acid) as the coupling component, metal complex formation occurs with the perihydroxy groups without oxidation.

Dyes with *o,o′*-hydroxycarboxyazo and *o,o′*-hydroxyaminoazo ligands are important for yellow shades. Anthranilic acid [118-92-3] is used advantageously with various couplers. *o,o′*-Hydroxyaminoazo dyes are also used to obtain green and brown shades. An example is Monochrome Brown EB [3564-15-6] (**58**) (CI Mordant Brown 1; CI 20110), an unsymmetrical primary disazo dye.

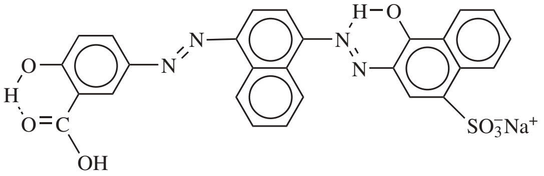


(**58**)

*Disazo Mordant Dyes.* Examples of disazo dyes are Diamond Alizarine Black SN [3258-74-0] (**59**) (CI Mordant Black 25; CI 21725) and a secondary disazo dye, Diamond Black F [8027-29-0] (**60**) (CI Mordant Black 5; CI 26695).



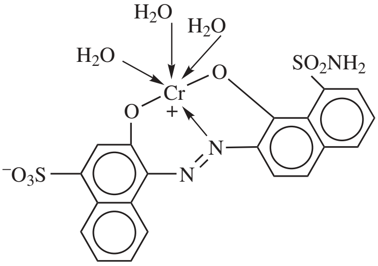
(**59**)



**(60)**

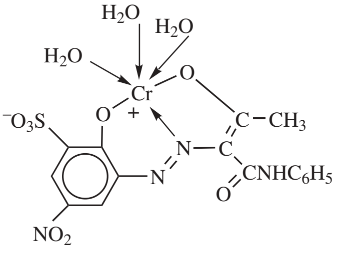
*Dyeing Procedures Employing Mordant Dyes.* In the chrome-mordant or chrome-bottom method, the wool is mordanted by immersion in a bath containing about 3% sodium dichromate and a small amount of, preferably, cream of tartar, or oxalic or formic acid, and by bringing to the boil; the chromate is reduced to the chromic state which combines with the wool. The mordanted goods are rinsed and immersed in a dyebath containing 1–8% acetic acid and are slowly brought to the boil. In the afterchrome or topchrome method, wool, after being dyed with a mordant dye, is aftertreated in acid solution with a chromium compound, generally dichromate. The metachrome or monochrome method, being a one-bath process, is simple and less expensive to use. Sodium chromate is added to the dyebath together with a salt of a strong acid and a weak base, such as ammonium sulfate, just before introduction of the fiber; mordanting and dyeing take place simultaneously. It has been found that the suitability for dyes of the one-bath (metachrome) method diminishes as the number of solubilizing groups increases (68).

*Premetallized Dyes.* Although discovered in 1912, the 1:1 chromium complexes known as Palatine Fast (BASF) and Neolan (Ciba) dyes had little practical use as wool dyes until 1920 when it was found that a strongly acidic dyebath (pH ca 2.0) (69) was required to obtain satisfactory dyeing and acceptable fastness properties. Dyes of this type exemplified by Neolan Blue 2G [6370-12-3] (**61**) (CI Acid Blue 158A; CI 15050) are still in use despite the damage to the wool caused by the strong acid in the dyebath.

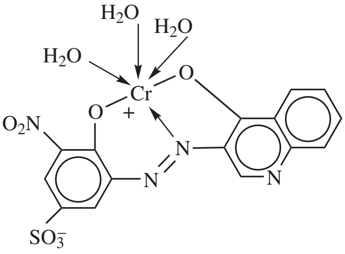


**(61)**

The use of acetoacetanilides and 2,4-dihydroxyquinolines as coupling components is demonstrated in the 1:1 chromium complexes Neolan Yellow GR [10343-58-5] (**62**) (CI Acid Yellow 99; CI 13900) (4−nitro−2−aminophenol ⟶ acetoacetanilide) and Palatine Fast Red BEN [6656-02-6] (**63**) (CI Acid Red 214; CI 19355) (2-amino-6-nitrophenol-4-sulfonic acid ⟶ 2,4-dihydroxyquinoline).



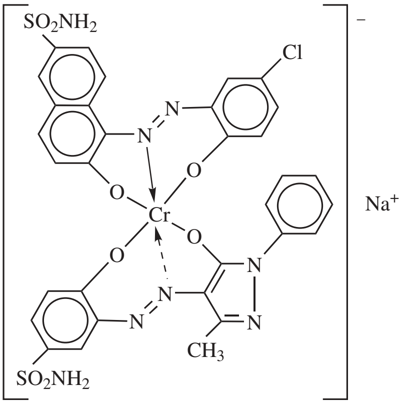
(**62**)



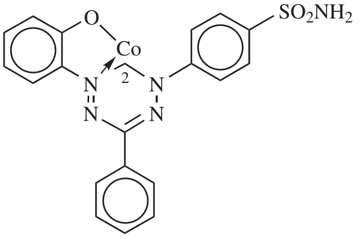
(**63**)

Under the low pH dyebath conditions, 2:1 complexes of the sulfo-containing types, disproportionate into a 1:1 complex and metal-free dye. At higher pH, 2:1 complexes are stable, but they do not yield level dyeings of dye to their ionized substituents ($SO_3^-$).

A notable advancement was the introduction in 1949 of Irgalan dyes by Geigy (70); a detailed historical review of this development was published (71). These dyes have excellent leveling properties and fastness to washing. Since they are dyed from neutral or slightly acidic (pH 5–7) dyebaths there is no adverse effect on wool. Chemically, these dyes are 2:1 chromium and cobalt complexes derived from *o,o*′-dihydroxyazo precursors having no substituents that are ionized in the 5–7 pH range (sulfo and carboxyl groups). To promote water solubility, this class of dyes generally contains nonionic water-solubilizing groups, such as alkylsulfonyl, sulfamyl, and acylamino. An example showing the use of methylsulfonyl groups to enhance water solubility is Irgalan Brown Violet DL (**52**). So-called mixed complexes (**64**) (1 mol dye A + 1 mol dye B + 1 mol metal ion) are valuable for obtaining homogeneous browns (72). The color of a cobalt complex is shifted hypsochromically relative to that of the analogous chromium complex. The Neopalatine Fast dyes (BASF) are mixed complexes from one colored terdentate ligand and one colorless bidentate ligand such as salicyclic acid (73).



(**64**)

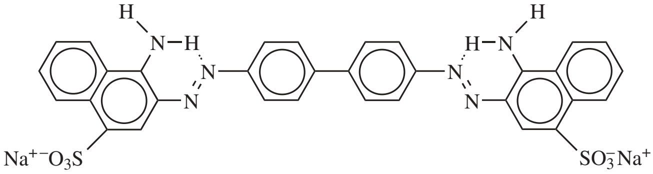


(**65**)

Another class of metal complex dyes is derived from the formazan structure. These dyes are applied to wool and nylon from a neutral or weakly acidic dyebath analogous to the 2:1 premetallized *o,o*′-dihydroxyazo complexes. The bluish-gray dye CI Acid Black 180 [11103-91-6] (**65**) (CI 13710) is a 2:1 cobalt complex of the formazan type.

The process and theory of dyeing is very complex (see DYES, APPLICATION AND EVALUATION). Dyes are held to the fiber by chemical interactions, by mechanical forces, as solid solutions, as insoluble particles dispersed in various media, or by a combination of these factors. The two most commonly occurring natural fibers, wool and cotton, exemplify the differences in dyeing theory and technique and the differences in dyestuff molecules required to meet these needs. Acid dyes, which are good wool dyes, as compared to the direct dyes for cotton show the following characteristics: acid dyes are quite soluble in dilute solutions and are much more soluble than direct dyes; solutions of direct dyes contain a large proportion of more complex micelles; and acid dyes have little or no affinity for pure cotton. The molecular weight of direct dyes is on the average much higher than that of acid dyes.

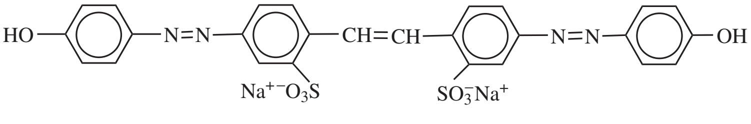
**5.3. Direct Dyes.** Direct dyes are defined as anionic dyes substantive to cellulosic fibers (cotton, viscose, etc), when applied from an aqueous bath containing an electrolyte. Before the discovery of Congo Red in 1884, only mordanted cotton could be dyed. Congo Red [573-58-0] (**66**) (CI Direct Red 28; CI 22120), a primary symmetrical disazo dye, which is made readily from bisdiazotized benzidine and naphthionic acid [84-86-6] (4-amino-1-naphthalenesulfonic acid), was the precursor of a most important line of dyes, including all shades, derived from benzidine and its homologues. Today, no benzidine dye is produced because benzidine is carcinogenic.



(**66**)

Direct dyes are one of the most versatile classes of dyestuff. In worldwide usage for cellulosic textiles, direct dyes are the second largest class of dyestuff. The important direct yellows and oranges of revealed chemical composition are listed in Table 7.

Three important direct yellows of revealed chemical composition belong to the stilbene class. Direct Yellow 11 (**24**) was mentioned earlier in the discussion of the condensation of nitro compounds. Another stilbene dye, Direct Yellow 4 (**67**), an old dyestuff discovered in 1886, is produced by coupling bisdiazotized 4,4′-diamino-2,2′-stilbenedisulfonic acid to two moles of phenol.

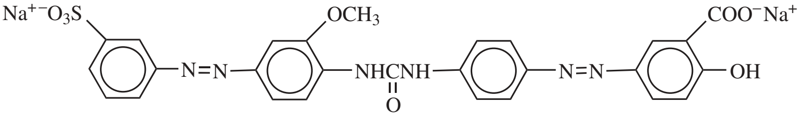


(**67**)

Table 7. **Yellow and Orange Shade Commercial Direct Dyes**

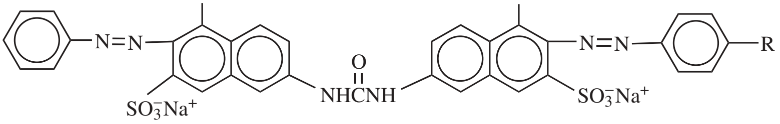
| CI name | Structure number | CAS Registry number | CI number | Chemical type |
|---|---|---|---|---|
| Direct Yellow 4 | (**67**) | [91-34-9] | 24890 | disazo |
| Direct Yellow 6 | | [1325-38-8] | 4000–40006 | stilbene |
| Direct Yellow 11 | (**24**) | [1325-37-7] | 40000 | stilbene |
| Direct Yellow 28 | (**23**) | [8005-72-9] | 19555 | thiazole |
| Direct Yellow 34 | | [15999-06-1] | 29060 | disazo |
| Direct Yellow 44 | (**68**) | [8005-52-5] | 29000 | disazo |
| Direct Yellow 106 | | [12222-60-5] | 40300 | stilbene |
| Direct Yellow 118 | | [12217-75-3] | 29042 | disazo |
| Direct Orange 6 | | [61814-85-5] | 23375 | disazo |
| Direct Orange 8 | | [2429-79-0] | 22130 | disazo |
| Direct Orange 15 | | [1375-35-5] | 40002–40003 | stilbene |
| Direct Orange 26 | (**71**) | [3626-36-6] | 29150 | disazo |
| Direct Orange 34 | | [12222-37-6] | 40215–40220 | stilbene |
| Direct Orange 39 | | [1325-54-8] | 40215 | stilbene |
| Direct Orange 72 | (**70**) | [12217-64-0] | 29058 | disazo |
| Direct Orange 102 | (**69**) | [6598-63-6] | 29156 | disazo |

Direct Yellow 44 (**68**) is prepared by phosgenation of an equimolar mixture of metanilic acid coupled to *o*-anisidinomethanesulfonic acid (with subsequent hydrolysis of the methanesulfonic acid group) and *p*-nitroaniline coupled to salicylic acid (with subsequent reduction of the nitro group).



(**68**)

*Direct Oranges.* All principal commercially produced direct oranges are of disazo or stilbene chemical composition (Table 7). Direct Orange 102 (**69**), is manufactured by first coupling aniline to 6,6′-ureylenebis-1-naphthol-3-sulfonic acid followed by a second coupling with *p*-aminobenzoic acid [150-13-0]. 6,6′-Ureylenebis-1-naphthol-3-sulfonic acid [134-47-4] is the coupling component in many of the most important direct colors. It is produced by phosgenation of two moles of J-acid (6-amino-1-naphthol-3-sulfonic acid).



(**65**) R=COO$^-$Na$^+$

(**70**) R=H

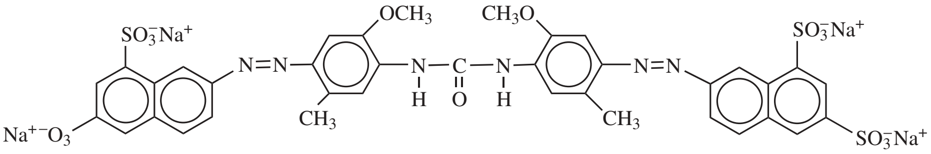
Other commercially important direct oranges include Direct Orange 26 (**70**) (2 mol aniline coupled to 6,6′-ureylenebis-1-naphthol-3-sulfonic acid), and Direct

Table 8. **Red Shade Commercial Direct Dyes**[a]

| CI name | Structure number | CAS Registry number | CI number |
|---|---|---|---|
| Direct Red 2 | (**73**) | [992-59-6] | 23500 |
| Direct Red 4 | | [6598-63-6] | 29165 |
| Direct Red 16 | | [6227-02-7] | 27680 |
| Direct Red 23 | (**74**) | [3441-14-3] | 29160 |
| Direct Red 24 | (**75**) | [6420-44-6] | 29185 |
| Direct Red 26 | | [3687-80-7] | 29190 |
| Direct Red 72 | (**76**) | [8005-64-9] | 29200 |
| Direct Red 73 | | [6460-01-1] | 29180 |
| Direct Red 80[b] | (**77**) | [2610-10-8] | 35780 |
| Direct Red 81 | (**72**) | [2610-11-9] | 28160 |
| Direct Red 83 | | [15418-16-3] | 29225 |

[a] Disazo, unless otherwise noted.
[b] Polyazo.

Orange 72 (**71**) which is obtained by phosgenating two moles of 7-amino-1,3-naphthalenedisulfonic acid [86-65-7] coupled to cresidine [120-71-8].

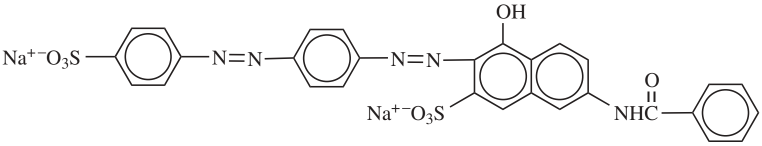


(**71**)

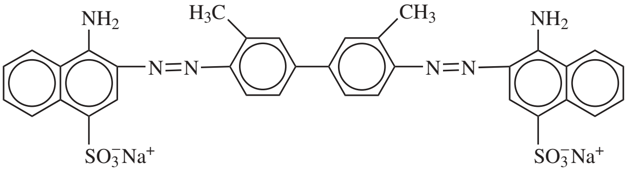
*Direct Reds.* The principal commercially produced direct reds, with revealed chemistry, are of disazo or polyazo composition (Table 8). Direct Red 81 (**72**) is manufactured by coupling *p*-(*p*-aminophenylazo)benzenesulfonic acid to *N*-benzoyl J-acid. Other important direct red dyes include those shown in Figure 20.

*Direct Blues.* Direct Blue 86, a phthalocyanine direct dye, represents a small but important segment of the direct dye structure groups. The dyes are brilliant greenish blue or turquoise shades. Table 9 and Figure 21 show some direct blues.

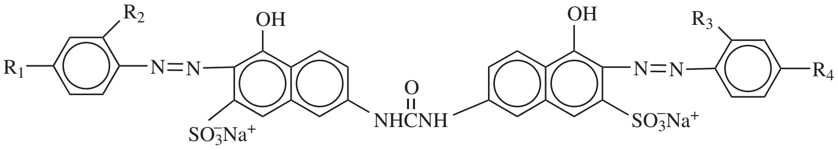
Direct Blue 218 is produced from Direct Blue 15 (**80**) by metallizing and elimination of methyl groups from the methoxide to form the copper complex. Direct Blue 15 (**80**) is prepared by coupling *o*-dianisidine [119-90-4] to two moles of H-acid (4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid) under alkaline pH conditions. Other important direct blues include Direct Blue 80 (**78**), *o*-dianisidine coupled to two moles of R-acid (3-hydroxy-2,7-naphthalenedisulfonic acid [148-75-4]) followed by metallizing to form a bis copper complex, and Direct Blue 22 (**77**), an asymmetrical disazo dye, prepared by coupling *o*-dianisidine to Chicago acid [82-47-3] and 2-naphthol. Direct Blue 75 (**82**) is an example of a trisazo dye represented as metanilic acid ⟶ 1,6-Cleve's acid ⟶ 1,6-Cleve's acid ⟶ (alk) *N*-phenyl J-acid.

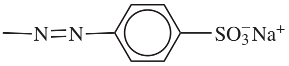


(**72**)
(**a**)

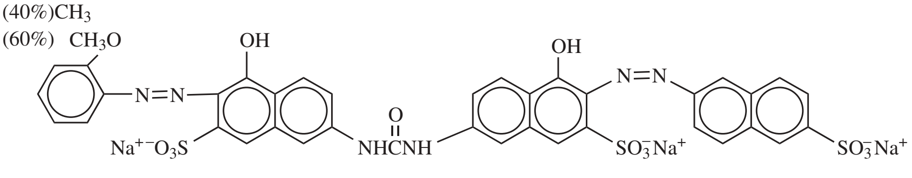


(**73**)
(**b**)



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| (**74**) | H | H | H | $NHCOCH_3$ |
| (**75**) | $SO_3^-Na^+$ | $CH_3$ | $OCH_3$ | H |
| (**76**) |  | $SO_3^-Na^+$ | $SO_3^-Na^+$ |  |

(**c**)

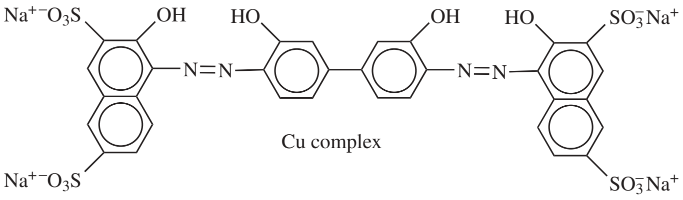


(**77**)
(**d**)

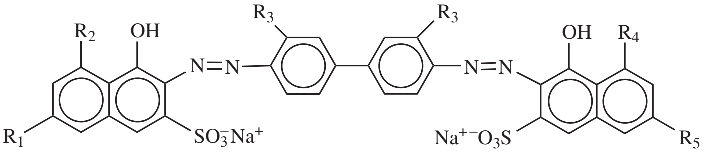
**Fig. 20.** Direct red dyes. (**a**) Direct Red 81 described in text (**72**); (**b**) Direct Red 2 (*o*-tolidine coupled to two moles of naphthionic acid) (**73**); (**c**) Direct Red 23 (aniline coupled to 6,6′-ureylenebis-1-naphthol-3-sulfonic acid with a second coupling with *p*-aminoacetanilide) (**74**); and Direct Red 80 (2 mol 6-amino-3,4′-azobenzenedisulfonic acid coupled twice to 6,6′-ureylenebis-1-naphthol-3-sulfonic acid) (**77**). Direct Red 24 (4-amino-*m*-toluenesulfonic acid coupled under acidic conditions to 6,6′-ureylenebis-1-naphthol-3-sulfonic acid followed by an alkaline coupling of *o*-anisidine) (**75**); (**d**) Direct Red 72 (Broenner's acid, ie, 6-amino-2-naphthalenesulfonic acid coupled under acidic conditions to 6,6′-ureylene-bis-1-naphthol-3-sulfonic acid followed by an alkaline coupling of a 3:2 mole ratio of *o*-anisidine and *o*-toluidine) (**76**).

Table 9. **Blue Shade Commercial Direct Dyes**

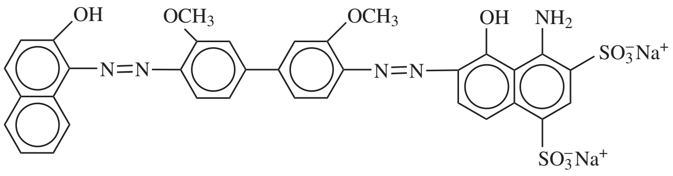
| CI name | Structure number | CAS Registry number | CI number | Chemical type |
|---|---|---|---|---|
| Direct Blue 15 | (**80**) | [2429-74-5] | 24400 | disazo |
| Direct Blue 22 | (**81**) | [2586-57-4] | 24280 | disazo |
| Direct Blue 25 | | [2150-54-1] | 23790 | disazo |
| Direct Blue 75 | (**82**) | [72245-54-6] | 34220 | trisazo |
| Direct Blue 76 | | [16143-79-6] | 24410 | disazo |
| Direct Blue 80 | (**78**) | [12222-00-3] | 24315 | disazo |
| Direct Blue 86 | | [1330-38-7] | 74180 | phthalocyanine |
| Direct Blue 98 | (**79**) | [6656-03-7] | 23155 | disazo |
| Direct Blue 108 | | [1324-58-9] | 51320 | oxazine |
| Direct Blue 218 | | [10401-50-0] | 24401 | disazo metallized |



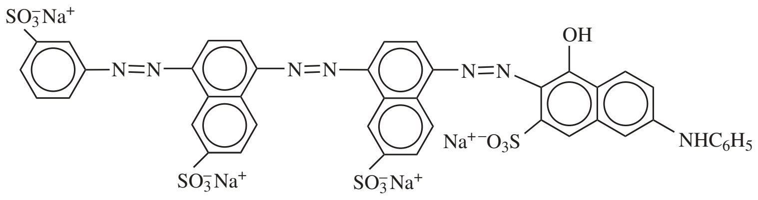
(**78**)



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| (**79**) | H | $SO_3^-Na^+$ | OH | H | $NHC_6H_5$ |
| (**80**) | $SO_3^-Na^+$ | $NH_2$ | $OCH_3$ | $NH_2$ | $SO_3^-Na^+$ |



(**81**)

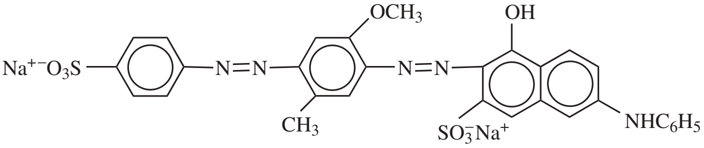


(**82**)

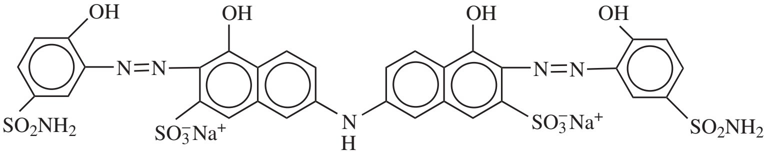
**Fig. 21.** Direct blue dyes.

*Direct Violets, Greens, Browns, and Blacks.* Direct violets and greens are small volume products.

Commercially important are CI Direct Violet 9 [6227-14-1] (**83**) (CI 27885) (sulfanilic acid coupled to cresidine followed by alkaline coupling to *N*-phenyl J-acid) and CI Direct Violet 66 [6798-03-4] (**84**) (CI 29120) (a copper complex of 2-amino-1-phenol-4-sulfonamide (2 mol) coupled to 6,6′-iminobis-1-naphthol-3-sulfonic acid).

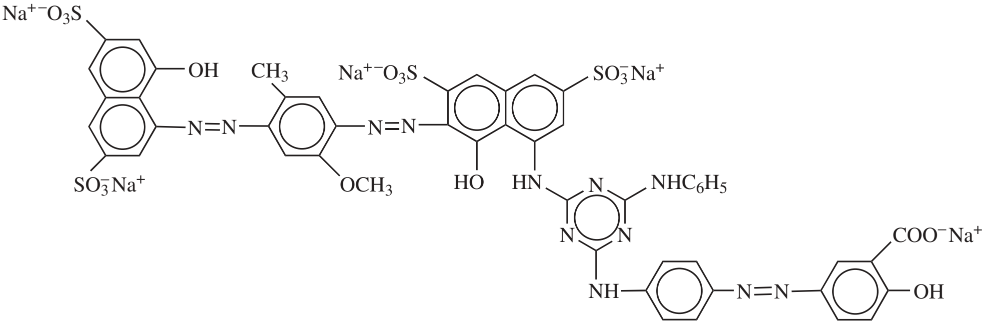


(**83**)



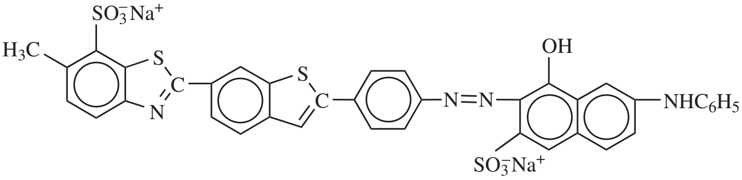
(**84**)

CI Direct Green 1 [3626-28-6] is of trisazo chemical composition shown previously. CI Direct Green 26 [6388-26-7] (**85**) (CI 34045) is produced through a combination of a blue and yellow dye components (H-acid is coupled to cresidine which is coupled to a coupling component; this coupling component is prepared by condensation of cyanuric chloride successively with H-acid, the azo dye obtained by reducing the nitro group in *p*-nitroaniline coupled to salicyclic acid, and aniline). Here the triazinyl group, similar to the —NH—CO—NH— group acts as a bridge and increases the substantivity and lightfastness. Brightness also results from the intramolecular combination as the triazinyl group protects the two different chromophoric systems from resonance interactions (74).

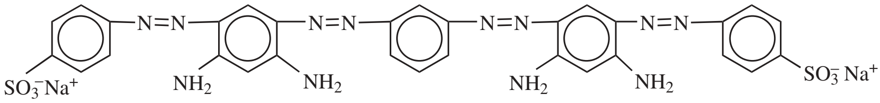


(**85**)

Two important browns, other than benzidine derivatives, are of azo chemical composition. Direct Brown 30 [6222-60-2] (**86**) (CI 17630) is produced by coupling Primuline [30133-37-2] (CI 49000) to *N*-phenylgamma acid under alkaline conditions. Direct Brown 44 [6252-62-6] (CI 35005-35010) is produced by coupling two moles of sulfanilic acid to Bismark Brown [10114-58-6] (Basic Brown 1) (CI 21000) forming a heterogeneous product with a significant component (**87**).

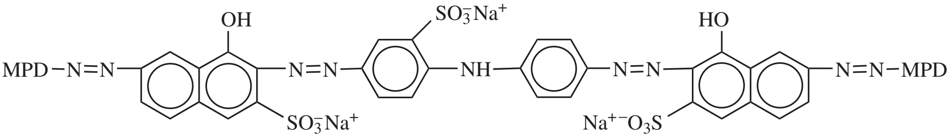


(**86**)



(**87**)

Direct Black 22 [6473-13-8] (**88**) (CI 35435) is produced first by coupling 4,4′diaminodiphenylamine-2-sulfonic acid to two moles of gamma acid to form a primary disazo dye, which is then bisdiazotized and coupled to two moles of *m*-phenylenediamine (MPD).



(**88**)

Table 10 lists some other direct blacks. Progress in the field of direct dyes is the development of reactant fixable dyes (indosol dyes). These dyes and the economics of dyeing processes have been reviewed (75,76).

*Azoic or Naphthol Dyes.* Azoic dyes (known also as ice colors and ingrain colors) are water-insoluble azo pigments, free from solubilizing groups, formed on the fiber by reaction of a diazo component with a coupling component, a so-called Naphthol AS compound, such as an arylide of 3-hydroxy-2-naphthoic

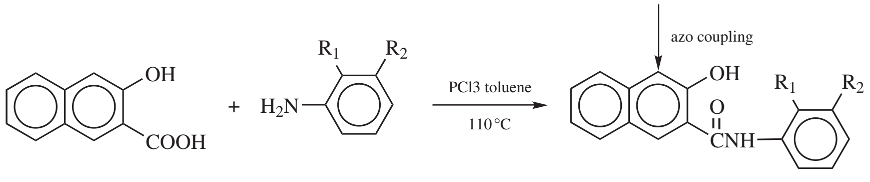
Table 10. **Black Shade Commercial Direct Dyes**

| CI name | CAS Registry number | CI number | Chemical type |
|---|---|---|---|
| Direct Black 19 | [6428-31-5] | 35255 | polyazo |
| Direct Black 22 | [6473-13-8] | 35435 | polyazo |
| Direct Black 150 | [6897-38-7] | 32010 | trisazo |
| Direct Black 166 | [57131-19-8] | 30026 | trisazo |

acid. The idea of producing insoluble azo dyes on the fiber was first patented in 1880, by chemists at Read Holliday & Sons, Ltd., in England, who impregnated cotton cloth with an alkaline solution of 2-naphthol and then coupled it with diazotized 2-naphthylamine to produce a bluish-red dyed fiber. The introduction in 1912 of Naphthol AS, so designated from Anilid Säure, German for acid anilide, was an event of great importance in the dyeing and printing industry. The discovery that 3-hydroxy-2-naphthoic acid arylides have greater substantivity for cotton than 2-naphthol, tremendously increased the range of bright and fast shades, and led to the introduction of an extensive line of Naphthol AS derivatives, fast color salts, rapid fast dyes, and the rapidogen dyes from diazoamino compounds.

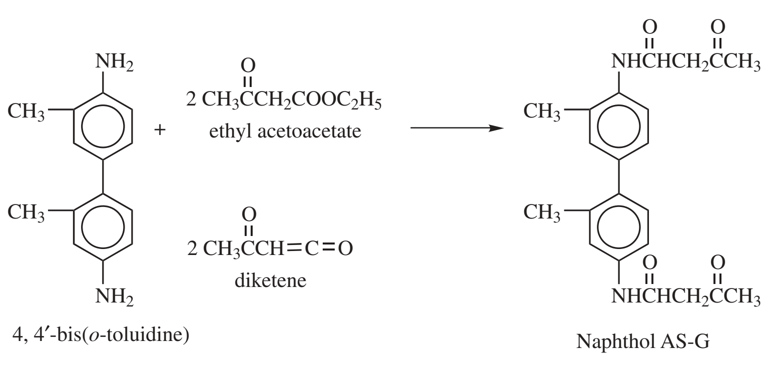
*Naphthol AS Coupling Components.* Naphthol AS components are the arylides of either *o*-hydroxyarylcarboxyclic acids or acylacetic acids. They are free of sulfo and carboxyl groups, but form salts with bases; these salts dissolve in water to give colloidal solutions, which couple with diazo components to form colored pigments. The whole class derives from the anilide of 3-hydroxy-2-naphthoic acid [92-70-6], Naphthol AS (**89**) (CI Azoic Coupling Component 2).

Naphthols of the *o*-hydroxyarylcarboxylic acid type are manufactured according to the equation:



| | (**89**) | (**90**) | (**91**) | (**92**) |
|---|---|---|---|---|
| $R_1$ | H | H | $CH_3$ | $OCH_3$ |
| $R_2$ | H | $NO_2$ | H | H |

In the production of arylides of acetoacetic acid, two methods are employed:



Commercially important coupling components include: Azoic Coupling Component 2 (3-hydroxy-2-naphthanilide [92-77-3]) (**89**); Azoic Coupling Component

Table 11. **Naphthol AS and Its Derivatives**

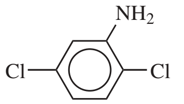
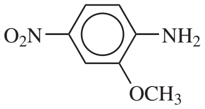
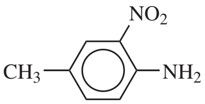
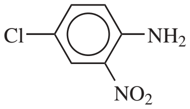
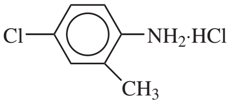
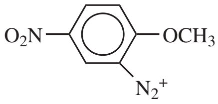
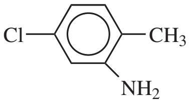
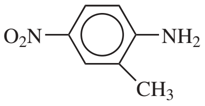
| CI azoic coupling component | CAS Registry number | CI number | Commercial name |
|---|---|---|---|
| 2 | [92-77-3] | 37505 | Naphthol AS |
| 3 | [91-92-9] | 37575 | Naphthol AS-BR |
| 4 | [132-68-3] | 37560 | Naphthol AS-BO |
| 7 | [135-64-8] | 37565 | Naphthol AS-SW |
| 9 | [4273-88-5] | 37625 | naphthanilide L4G |
| 12 | [92-72-8] | 37550 | Naphthol AS-ITR |
| 14 | [92-74-0] | 37558 | Naphthol AS-PH |
| 16 | [132-62-7] | 37605 | Naphthol AS-DB |
| 17 | [135-65-9] | 37515 | Naphthol AS-BS |
| 18 | [135-61-5] | 37520 | Naphthol AS-D |
| 20 | [135-62-6] | 37530 | Naphthol AS-OL |
| 29 | [92-75-1] | 37527 | Naphthol AS-MX |
| 34 | [137-52-0] | 37531 | Naphthol AS-CA (naphthanilide EL) |

17, Naphthol AS-BS, (3-hydroxy-3-nitro-2-naphthanilide) (**90**); Azoic Coupling Component 18, Naphthol AS-D, (3-hydroxy-2-methyl-2-naphthanilide) (**91**); and Azoic Coupling Component 20, Naphthol AS-OL, (3-hydroxy-2′-methoxy-2-naphthanilide) (**92**) (Table 11).

*Fast Color Salts.* In order to simplify the work of the dyer, diazonium salts, in the form of stable dry powders, were introduced under the name of fast color salts. When dissolved in water they react like ordinary diazo compounds. These diazonium salts, derived from amines, free from solubilizing groups, are prepared by the usual method and are salted out from the solutions as the sulfates, the metallic double salts, or the aromatic sulfonates. The isolated diazonium salt is sold in admixture with anhydrous salts such as sodium sulfate or magnesium sulfate.

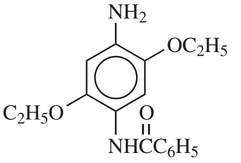
Commercially, the most important fast color bases (Table 12) and salts include: Azoic Diazo Component 3, produced by the reduction of 1,4-dichloro-2-nitrobenzene; Azoic Diazo Component 5, produced by nitration of *o*-acetanisidide with subsequent hydrolysis; Azoic Diazo Component 8, produced by nitration of *p*-acetotoluidide in $H_2SO_4$ and subsequent saponification; Azoic Diazo Component 9, produced by selective ammonolysis of 1,4-dichloro-2-nitrobenzene; Azoic Diazo Component 11, produced by chlorination of *o*-acetotoluidide and subsequent saponification; Azoic Diazo Component 13, produced either by partial reduction of 2,4-dinitroanisole or nitration of *o*-anisidine; Azoic Diazo Component 20 (4′-amino-2′,5′-diethoxybenzanilide) (**93**), produced by condensation of 2,5-diethoxyaniline with benzoyl chloride, followed by nitration and reduction; Azoic Diazo Component 32, produced by nitration of *p*-chlorotoluene followed by reduction of the resulting 4-chloro-2-nitrotoluene; and Azoic Diazo Component 34, produced by nitration of *o*-benzenesulfonotoluidide followed by hydrolysis. Variamine Blue B the half sulfate [6254-98-4] of (**94**), ie, Azoic Diazo Component 35 used for dark blue or green shades is marketed as the free base or half sulfate. It is produced by condensation of *p*-anisidine with 2-chloro-5-

Table 12. **Fast Color Bases**

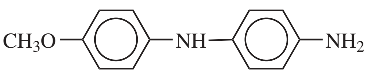
| CI azoic diazo component | Amine structure | CAS Registry number | CI number | Fast base or salt |
|---|---|---|---|---|
| 1 | | [96-96-8] | 37135 | Bordeaux GP |
| 3 |  | [95-82-9] | 37010 | Scarlet GG |
| 5 |  | [97-52-9] | 37125 | Red B |
| 8 |  | [89-62-3] | 37110 | Red GL |
| 9 |  | [89-63-4] | 37040 | Red 3GL |
| 10 | | [4274-03-7] | 37120 | Red RC |
| 11 |  | [3165-93-3] | 37085 | Red TR |
| 12 | | [99-55-8] | 37105 | Scarlet G |
| 13 |  | [27165-17-9] | 37130 | Scarlet R |
| 14 | | [80-22-8] | 37175 | Red PDC |
| 20 | (**93**) | [120-00-3] | 37175 | Blue BB |
| 32 |  | [6259-42-3] | 37090 | Red KB |
| 34 |  | [99-52-5] | 37100 | Red RL |
| 35 | (**94**) | [6254-98-4] | 37255 | Blue VB[a] |
| 41 | | [99-21-8] | 37165 | Violet B |
| 42 | | [97-35-8] | 37150 | Red ITR |
| 44 | | [137-04-2] | 37000 | Yellow GC |
| 48 | | [20282-70-6] | 37235 | Blue B |
| 49 | | [121-50-6] | 37050 | Orange RD |
| 109 | | [6369-04-6] | 37245 | Black BN |

[a] Variaminblue B.

nitrobenzenesulfonic acid, reduction, and desulfonation of the resulting 5-amino-2-*p*-anisidinobenzenesulfonic acid.



(**93**)



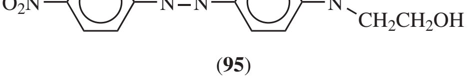
(**94**)

*Applications of Naphthol AS Compounds and Fast Color Salts.* For dyeing, the Naphthol AS is dissolved in water with base and diluted to the proper concentration. The cloth is passed through the solution and squeezed. The degree of squeezing together with the concentration of the Naphthol AS determines the depth of the final color. After impregnation, the material, which may or may not be dried, is passed into a cold solution of a fast color salt or diazotized amine, where practically instantaneous coupling takes place and the insoluble dye is formed on the material. After coupling, the material is passed through squeeze rolls, washed with cold water to remove all unreacted diazo compound, and washed in boiling soap solution to develop the true shade and improve fastness.

For printing, the naphthol and the fast color salts are coupled as for dyeing, but by different mechanical means. In one important method the cloth is naphtholated as for dyeing. The material is then dried and passed through the printing machine. To obtain multicolor prints, each roller of the printing machine prints a paste containing a different fast color salt. The cloth is dried again, aged in either neutral or acid steam, washed, soaped to remove the uncombined Naphthol AS from the unprinted part of the material, and dried, leaving a colored print on a white background.

In order to eliminate the expensive naphtholating and drying operations some further important developments were introduced by Chemische Fabrik Griesheim-Elektron under the names of Rapid Fast, Rapidazol, and Rapidogen combinations (mixtures of substantive coupling components with antidiazotates, diazosulfonates, and diazoamino compounds, respectively).

**5.4. Disperse Azo Dyes.** *Commercial Disperse Azo Dyes.* The first proposal to use insoluble dyes in suspension in an aqueous foam bath, ie, disperse dyes, to dye cellulose acetate was in 1921 (77). Commercialization of disperse dyes began in 1924 with the introduction of the Duranol dyes by British Dyestuffs Corporation (78) and the SRA dyes by British Celanese Company (79). In contrast to the acid monoazo dyes, derivatives of benzene rather than of naphthalene are of the greatest importance as coupling components. Among these components mono- and dialkylanilines (especially *N*-β-hydroxyethyl- and *N*-β-acetoxyethylaniline derivatives) are widely used couplers. Nitrodiazobenzenes are widely used as diazo components. A typical example is Celliton Scarlet B [2872-52-8] (**95**) (CI Disperse Red 1; CI 11110).



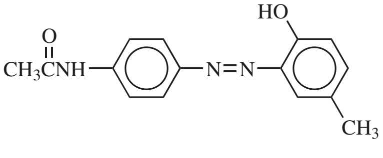
(**95**)

Table 13. **Yellow and Orange Shade Commercial Disperse Dyes**

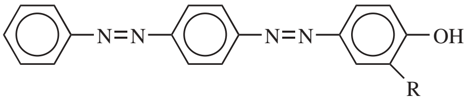
| CI name | Structure number | CAS Registry number | CI number |
|---|---|---|---|
| Disperse Yellow 3 | (**96**) | [2832-42-8] | 11855 |
| Disperse Yellow 4 | | [6407-80-3] | 12770 |
| Disperse Yellow 5 | | [6439-53-8] | 12790 |
| Disperse Yellow 7 | (**97**) | [6300-37-4] | 26090 |
| Disperse Yellow 8 | | [6358-49-2] | 12690 |
| Disperse Yellow 10 | | [8005-71-8] | 12795 |
| Disperse Yellow 23 | (**98**) | [6250-23-3] | 26070 |
| Disperse Yellow 60 | | [15790-15-5] | 12712 |
| Disperse Orange 1 | | [2581-69-3] | 11080 |
| Disperse Orange 3 | | [730-40-5] | 11005 |
| Disperse Orange 5 | | [6232-56-0] | 11100 |
| Disperse Orange 13 | (**99**) | [6253-10-7] | 26080 |
| Disperse Orange 25 | (**101**) | [31482-56-1] | 11227 |
| Disperse Orange 29 | (**100**) | [19800-42-1] | 26077 |
| Disperse Orange 30 | | [5261-31-4] | 11119 |
| Disperse Orange 56 | | [67162-11-2] | 12650 |
| Disperse Orange 62 | | [37672-70-1] | 11239 |
| Disperse Orange 138 | | [43047-20-7] | 11145 |

Generally speaking, disperse dyes for acetate possess only moderate fastness to gas, light, sublimation (heat), and washing. There were no suitable blue azo disperse dyes available in early years and, as a consequence, aminoanthraquinone types gained prominence in this shade range. The latter, however, were subject to gas fading, ie, on exposure to oxides of nitrogen and ozone acetate dyed blue became pink. This deficiency led to the development of many antigas fading additives. Commercially important disperse yellow and orange dyes for which chemical structures are revealed by the producers are listed in Table 13.

The early yellow disperse dyes were based on phenolic coupling components, eg, CI Disperse Yellow 3 (**96**) (diazotized 4-aminoacetanilide coupled to *p*-cresol) which is still used today for the coloration of cellulose acetate and nylon fibers.

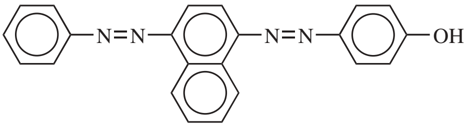


(**96**)

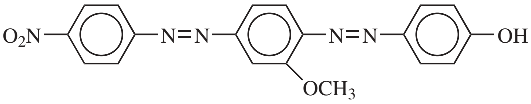


(**97**) R = $CH_3$
(**98**) R = H

Disperse Yellow 7 (**97**) and Disperse Yellow 23 (**98**) are two disazo dyes which are manufactured by diazotizing *p*-phenylazoaniline [60-09-3] (CI 11000) followed by coupling to *o*-cresol and phenol, respectively. Among the azo colors of orange shades, Disperse Orange 13 (**99**) and Disperse Orange 29 (**100**) are two disazo dyes containing phenol as coupling components.

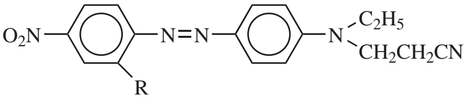


(**99**)



(**100**)

Other disperse azo colors produced in the United States of revealed chemical constitution are listed in Table 14.



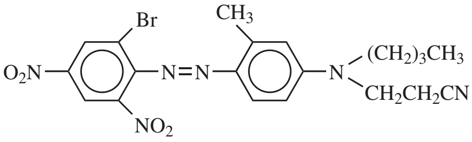
(**101**) R = H
(**102**) R = CN

Disperse reds are second only to blues as the most important disperse color manufactured. All commercial disperse reds are monoazo dyes. Disperse Violet 24 (**103**) is produced from diazotized 2-bromo-4,6-dinitroaniline by coupling

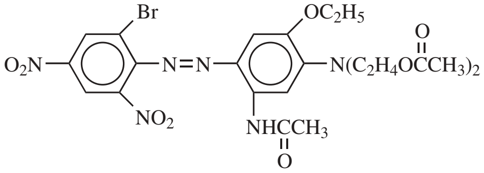
Table 14. **Commercial Disperse Dyes**

| CI name | Structure number | CAS Registry number | CI number |
|---|---|---|---|
| Disperse Red 1 | (**95**) | [2872-52-8] | 11100 |
| Disperse Red 5 | | [3769-57-1] | 11215 |
| Disperse Red 7 | | [4540-00-5] | 11150 |
| Disperse Red 13 | | [3180-81-2] | 11115 |
| Disperse Red 17 | | [3179-89-3] | 11210 |
| Disperse Red 19 | | [3003-33-6] | 11130 |
| Disperse Red 31 | | [2475-43-6] | 11250 |
| Disperse Red 32 | | [3084-21-7] | 11190 |
| Disperse Red 58 | | [6373-93-9] | 11135 |
| Disperse Red 65 | | [16586-43-9] | 11228 |
| Disperse Red 72 | | [12223-39-1] | 11114 |
| Disperse Red 73 | (**102**) | [16889-10-4] | 11116 |
| Disperse Red 90 | | [27767-98-2] | 11117 |
| Disperse Violet 24 | (**103**) | [6374-03-4] | 11200 |
| Disperse Violet 33 | | [66882-16-4] | 11218 |
| Disperse Blue 11 | (**106**) | [6358-51-6] | 11260 |
| Disperse Blue 79 | (**104**) | [12239-34-8] | 11345 |
| Disperse Blue 165 | | [41642-51-7] | 11077 |
| Disperse Blue 183 | | [2309-94-6] | 11078 |
| Disperse Brown 1 | (**105**) | [23355-64-8] | 11152 |
| Disperse Black 1 | (**107**) | [6054-48-4] | 11365 |

with 2-(*N*-butyl-*m*-toluidine)ethanol.



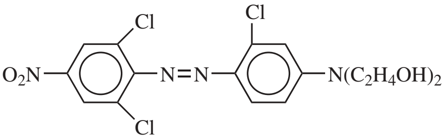
(**103**)



(**104**)

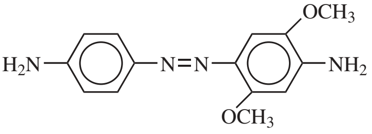
Blues are the single most important color in the disperse class, both in terms of amounts produced and dollar sales volume. Among all dyes, Disperse Blue 79 (**104**) (6-bromo-2,4-dinitroaniline [1817-73-8] coupled to 3-bis-(2-acetoxyethyl)-amino-*p*-acetophenetidine [20249-05-2]) was the highest volume dye in the late 1980s and continues.

The only disperse brown of commercial importance is Disperse Brown 1 (**105**). A method still in use to produce navy and black shades economically on acetate involves formation of the dye directly on the substrate (azoic dyeing).

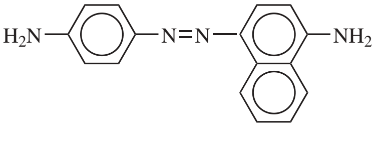


(**105**)

Monoazo dyes such as Disperse Blue 11 (**106**) and Disperse Black 1 (**107**) are applied to cellulose acetate as a dispersion and dyed in the usual way, then diazotized *in situ* and coupled in this instance, to 3-hydroxy-2-naphthoic acid forming the blue and black shades, respectively.

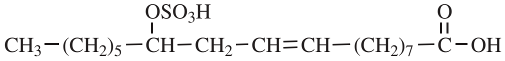


(**106**)



(**107**)

*Dispersion Technology.* Substantial advancements in dispersion technology have been made since the initial introduction in 1923 of disperse dyes in paste form for cellulose acetate. Dyes were dissolved in sulfonated fatty acids such as sulforicinoleic acid [36634-48-7] (SRA), 12-hydroxy-9-octadecenoic acid sulfate (**104**), and then formed into a dispersed paste by mixing the solution with water giving rise to an entire line of SRA dyes for acetate (80). The Duranol dyes (61) were prepared by grinding or dissolving aminoanthraquinone dyes in a solvent followed by drowning into water containing soap or Turkey Red Oil.



$$CH_3-(CH_2)_5-\overset{\displaystyle OSO_3H}{\overset{|}{C}}H-CH_2-CH=CH-(CH_2)_7-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

(**108**)

Manufacturing procedures for producing dye dispersions are generally not disclosed. The principal dispersants in use include long-chain alkyl sulfates, alkaryl sulfonates, fatty amine–ethylene oxide condensates, fatty alcohol–ethylene oxide condensates, naphthalene–formaldehyde–sulfuric acid condensates, and the lignin sulfonic acids.

All dispersions are thermodynamically unstable, since the interfacial area and hence the surface energy tend to decrease, ie, agglomeration occurs. The primary function of dispersing agents is to stabilize dispersions. Anionic dispersing agents, such as the lignosulfonates, are adsorbed on the minute dye particles creating negatively charged surfaces. On close approach the particles then tend to repel each other preventing rapid agglomeration and thereby promoting dispersion stability. A significant development has been production of dispersing agents which confer improved dispersion stability at elevated temperatures and in the case of lignin dispersants (81) products with less tendency to stain the fiber or cause reduction of the dye have been introduced. An excellent review of developments in disperse dye technology has been given (82).

Various mechanical means of reducing the dye particle size have been employed to improve the quality of dispersions. An early process in Germany, and now outmoded, involved kneading a viscous taffylike aqueous paste mixture of dyestuff and dispersing agent in a mixer containing two heavy, closely fitting sigmoid blades. The blades turning at different speeds in opposite directions created a shearing action to break down the dye crystals. This method was largely replaced by the ball mill. Generally, the wet dye filter cake, dispersing agent, and some water are added into the ball mill which is a large horizontal, steel, cylindrical tank partially filled with ceramic balls. The cylinder is rotated for a period of time sufficient for the balls to grind the dye to the desired particle size.

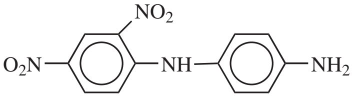
A highly efficient device now in widespread use is the sand mill, which consists of a vertically cylindrical tank equipped with a specially designed impeller and containing sand. The aqueous dye slurry being pumped into the cylinder is subjected to the high shearing action of the swirling sand (83). Other grinding media, such as glass beads, carborundum, and zircon, can be used in place of sand. Sand mills can be the open type with the dye slurry flowing out by gravity or the closed type in which the dye slurry throughput is constantly under pressure. Modern dispersion machinery and methods for the evaluation of dye dispersions have been described (84).

Disperse dyes are sold in liquid form as aqueous pastes, or in powder form (by spray drying). The particle size distribution of commercial disperse dyes is mostly in the range of 1–2 μm which is a decided improvement when compared with the fineness of the early disperse dyes for acetate. Disperse dyes are now formulated to withstand longer term exposure to the prevailing higher dyeing temperatures and must pass stringent filtration and dyeing tests before they are offered for sale. Disperse dyes in liquid form contain additives and stabilizers to prevent settling, freezing and drying out, and control foaming. Since practically all dyes are dispersed by wet-milling processes, spray drying is used to obtain dye powders. In addition to the additives and stabilizers in the liquid types, the powder brands are either treated or prepared in the form of grains to minimize dusting in handling (85).

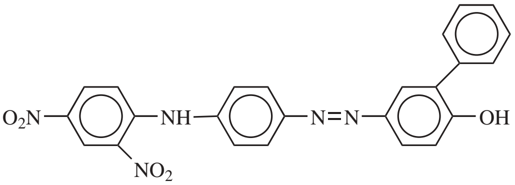
*Application Techniques, Structural Variations, and Fastness Properties.* When applied to polyester fiber, many of the disperse dyes originally developed for cellulose acetate were found to be deficient in lightfastness, build-up properties, and especially fastness to the high temperatures employed in the newer dyeing and finishing, printing, and Thermosol (dry heat) processes.

Since 1950, there has been a steady development of new disperse dyes to meet the demands imposed by the changing application methods and to provide the much needed improvement in fastness properties. Six different methods of applying disperse dyes have been developed since the introduction of polyester fibers (86): (*1*) Dyeing at the boil in the presence of a carrier is used for delicate fabrics, polyester–wool blends, etc. (*2*) Dyeing at 120–135°C in pressurized vessels gives better exhaustion and often improved fastness to light, rubbing, and perspiration. (*3*) Thermofixation techniques at 190–220°C are used for the continuous processing of certain types of fabrics. (*4*) Transfer printing, generally at 210°C for 30 seconds, is an important development. (*5*) Solvent dyeing methods are available, but are not popular. (*6*) Printing and continuous dyeing processes have been developed for polyester–cotton blends using specialist dyes and application techniques such as the Dybln (DuPont), Cellestren (BASF), and Dispersol (ICI) ranges.

Disperse dyes are classified as high energy or low energy types (87). The use of higher dyeing temperatures for polyester fibers compared with those used for cellulose acetate has made possible the use of dyes of higher molecular weight, the so-called high energy dyes. The sublimation fastness has been improved by increasing the molecular size. For example, an existing dye, CI Disperse Yellow 9 [6373-73-5] (**109**) (CI 10375) has been diazotized and coupled to a substituted phenol to give CI Disperse Yellow 70 [12223-91-5] (**110**) (CI 11900) which has better sublimation fastness. Low energy dyes have lower fastness to sublimation, diffuse rapidly into the fiber, and readily produce level dyeings at lower temperatures.



(**109**)

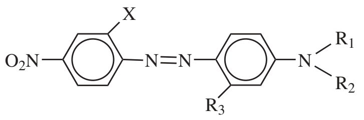


(**110**)

High energy dyes are required in the Thermosol application and in those instances in which the dyed fabric is subjected to a heat-setting treatment. Each energy type has a characteristic rate of exhaust and, as a consequence, only disperse dyes of the same energy class are used in mixes for shade matching purposes.

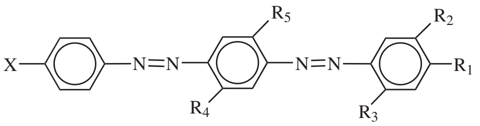
A use for disperse dyes which has undergone rapid growth since 1970 is in inks for the heat-transfer printing of polyester, especially double knit fabrics. This simple method consists of printing the desired design on paper and then transferring the design from the paper to the fabric with heat. In the heat-transfer process the dye volatilizes, is adsorbed onto the fiber surface, and then diffuses into the fiber. Generally low and medium energy types are used for this purpose. To make color mixes, dyes with the same transfer rate, not necessarily the same energy class, must be selected. There are three main groups of azo disperse dyes. A selection of aminoazobenzene and disazo dye structures (**111–119**) for coloring polyester appears in Figure 22 (88).

*Monoazo dyes*



| Structure Number | Color | X | R₁ | R₂ | R₃ | CAS Registry Number | Reference |
|---|---|---|---|---|---|---|---|
| (**111**) | orange | H | $CH_2CH_2CN$ | $CH_2CH_2CN$ | H | [*4234-72-4*] | 89 |
| (**112**) | scarlet | Cl | $CH_2CH_2CN$ | $CH_2CH_2OCOCH_3$ | H | [*6021-61-1*] | 90 |
| (**113**) | red | $SO_2CH_3$ | $CH_2CH_2OCOCH_3$ | $CH_2CH_2OCOCH_3$ | H | [*26692-47-6*] | 91 |
| (**114**) | dark red | Cl | $CH_2CH_2CN$ | $CH_2CH_3$ | $NHCOCH_3$ | [*65605-39-2*] | 92 |
| (**115**) | rubine | CN | $CH_2CH_2CN$ | $CH_2CH_2OCOCH_3$ | H | [*65605-40-5*] | 90 |

*Disazo dyes*



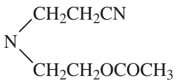
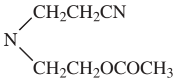
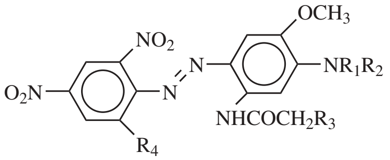
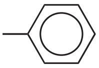
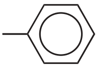
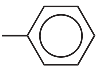
| Structure Number | Color | X | R₁ | R₂ | R₃ | R₄ | R₅ | Reference |
|---|---|---|---|---|---|---|---|---|
| (**116**) | yellow | $NHCOCH_3$ | OH | H | H | $CH_3$ | H | 93 |
| (**117**) | orange | $NO_2$ | OH | $CH_3$ | H | $CH_3$ | H | 94 |
| (**118**) | yellowish red | H |  $N(CH_2CH_2CN)(CH_2CH_2OCOCH_3)$ | H | $NHCOCH_3$ | H | H | 95 |
| (**119**) | red | $NO_2$ |  $N(CH_2CH_2CN)(CH_2CH_2OCOCH_3)$ | H | H | H | H | 96 |

**Fig. 22.** Azo disperse dyes for polyester.

All of the disperse dyes for polyester shown in Figure 22 are reported to have high resistance to sublimation, good lightfastness, and good build-up of color. Generally the dye structures have been modified to achieve these desirable properties by either increasing the molecular weight or introducing more polar groups, or both, and by decreasing further their slight solubility in water. The hydrophilic *N*-β-hydroxyethyl group present in each of the acetate disperse dyes (**95**), (**103**), and (**105**) is not to be found in the structures (**111–119**). At the higher temperatures employed in the dyeing of polyester, dyes containing the *N*-β-hydroxyethyl moiety have increased water-solubility, do not exhaust completely from the dye liquor, and as a consequence lack good build-up. Also, aminoazobenzene disperse dyes containing *N*-β-hydroxyethyl groups have relatively poor lightfastness on polyester. These shortcomings can be overcome by acylation of the hydroxyl group to form, eg, the *N*-acetoxyethyl group present in a number of the structures in Figure 22. The introduction of the polar *N*-β-cyanoethyl group into the molecule yields dyes with good fastness to light and sublimation. The combination of *N*-β-cyanoalkyl and *N*-β-acyloxyalkyl groups in a coupling component for disperse azo dye is particularly advantageous (97).

The use of three electron-withdrawing groups in the 2-, 4-, and 6-positions of the diazo component and two electron-donating groups in the 2- and 5-positions of the aminobenzene coupler has afforded blue azo disperse dyes for polyester with excellent build-up, good fastness to sublimation, and moderate to good lightfastness. Compared with aminoanthraquinone blue dyes, these dyes are relatively dull in shade and not as lightfast. However, the azo types are used with success in heavy navy and black shades (97). Besides Disperse Blue 79 (**104**), other representative chemical structures (**120–123**) for blue azo disperse dyes are as follows:



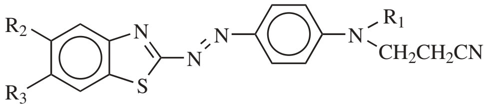
| | R$_1$ | R$_2$ | R$_3$ | R$_4$ | CAS Registry Number |
|---|---|---|---|---|---|
| (**120**) | CH$_2$CH$_2$OCH$_2$CH$_2$CN | CH$_2$CH$_2$OCH$_2$CH$_2$CN | H | Cl | [16539-95-0] |
| (**121**) | CH$_2$  | CH$_2$  | H | CN | [52583-51-4] |
| (**122**) | CH$_2$CH$_2$OCH$_2$CH$_2$CN | CH$_2$  | CH$_3$ | Cl | [65605-44-9] |
| (**123**) | CH$_2$CH$_2$CN | C$_2$H$_5$ | H | Br | [22578-86-5] |

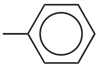
The patented method of preparation of the blue dye (**124**) [19187-01-0] (98) involves treating the analogous dibromo substituted azo dye with cuprous cyanide in dimethylformamide or *N*-methylpyrrolidinone at 50°C to effect replacement of the two bromo substituents by cyano groups.

(**124**)

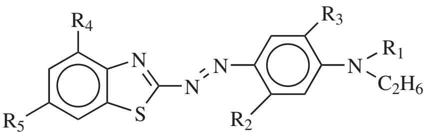
The greenish-blue dye (**121**) (99) is prepared in a similar fashion, replacing bromo with cyano by using cuprous cyanide, pyridine, and 2-methoxyethanol as solvent at 85°C.

*Heterocyclic Disperse Dyes.* Diazotizable aminoheterocyclic compounds are also used in the production of disperse dyes. Examples of the important class of 2-aminobenzothiazole dyes follow. Red shades include compounds (**125–127**):



| | $R_1$ | $R_2$ | $R_3$ | CAS Registry Number | Reference |
|---|---|---|---|---|---|
| (**125**) | $C_2H_5$ | Cl | Cl | *[25176-89-0]* | 100 |
| (**126**) | $CH_2$  | H | $NO_2$ | *[65605-45-0]* | 101 |
| (**127**) | $CH_2CH_2OOCCH_3$ | H | $SO_2CH_3$ | *[54983-30-1]* | 102 |

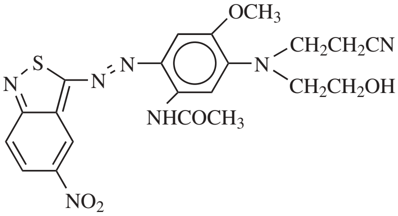
(**128**) is bluish red and (**129**) is bright blue.



| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | | Reference |
|---|---|---|---|---|---|---|---|
| (**128**) | $CH_2CH_2OOCC_6H_5$ | $CH_3$ | H | H | $SO_2CH_3$ | *[43042-04-2]* | 103 |
| (**129**) | $C_2H_5$ | $NHCOCH_3$ | $OCH_3$ | $OCH_3$ | $NO_2$ | *[19433-87-5]* | 104 |

The absorption spectra, and fastness properties of a number of substituted aniline dyes have been compared with those of the similarly substituted benzothiazolylazo dyes (105). For instance, the dye prepared from 4-nitroaniline [100-01-6] and a given coupler was compared with the dye made from 2-amino-6-nitrobenzothiazole [6285-57-0] and the same coupler since 4-nitroaniline yields 2-amino-6-nitrobenzothiazole on treatment with potassium thiocyanate and bromine in acetic acid. The benzothiazolylazo dyes are deeper in shade (bathochromic) and have higher absorptivities, ie, greater tinctorial strength than their phenylazo counterparts. Further, the benzothiazole types generally have higher fastness to light fading and exhibit definitely superior sublimation fastness.

A large bathochromic shift is observed in the blue-green dye (**130**) [65605-46-1] (106) prepared from the diazo component 3-amino-5-nitro-2,1-benzisothiazole.

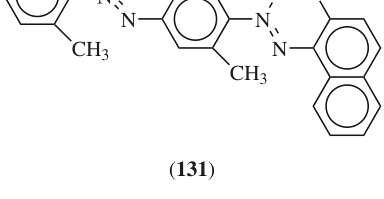


(**130**)

Couplers which form scarlet dyes with 4-nitroaniline and red dyes with 2-amino-6-nitrobenzothiazole yield blue dyes with 3-amino-5-nitro-2,1-benzisothiazole [14346-19-1].

A number of other heterocyclic diazo components such as thiazole, indazole, thiophenes, and thiadiazole types as well as heterocyclic couplers, ie, 6-hydroxy-2-pyridinone [626-06-2], barbituric acid [67-52-7], and tetrahydroquinoline [25448-04-8] have been cited in the literature (107,108). Reviews on disperse dyes have been published (109,110).

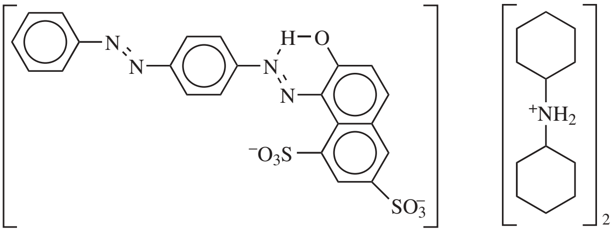
**5.5. Oil Soluble Azo Dyes.** The oil soluble, water-insoluble, azo dyes dissolve in oils, fats, waxes, etc. Generally, yellow, orange, red, and brown oil colors are azo structures and greens, blues, and violets are primarily anthraquinones (see DYES, ANTHRAQUINONE). Blacks are usually nigrosines and indulines of the azine type (see AZINE DYES). An example is Oil Red [85-83-6] (**131**) (CI Solvent Red 24; CI 26105). Uses include the coloring of hydrocarbons, waxes, oils, candles, etc.



(**131**)

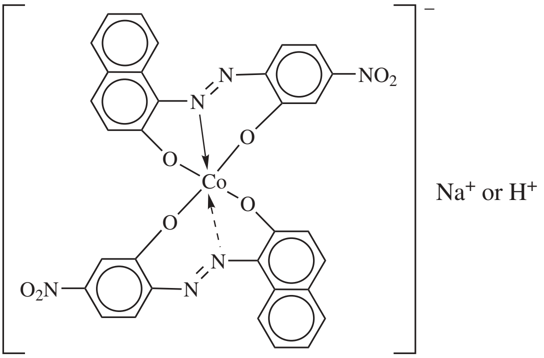
Substitution by chloro, nitro, and similar groups increases the molecular weight and improves sublimation fastness but lowers the oil solubility of this group of dyes.

**5.6. Spirit Soluble Azo Dyes.** Spirit-soluble azo dyes dissolve in polar solvents, such as alcohol and acetone, and find application in the coloring of lacquers, plastics, printing inks, and ball-point pen inks. Of the two principal types of azo structures used, the most important are the insoluble salts of azo dyes containing sulfo groups and relatively complex organic amines. Mono- and dicyclohexylamine, isoamylamine, and the arylguanidines (111) often serve as the amine, and the anionic component is chosen from the class of acid dyes for wool. An example is Zapon Fast Scarlet CG [5413-75-2] (**132**) (CI Acid Red 73; CI 27290).



(**132**)

The second type is comprised of 2:1 metal complexes of *o,o′*-dihydroxy azo dyes which generally do not contain sulfo or other strongly hydrated groups as found in the premetallized 2:1 complexes for wool. Thus their solubility in esters, ketones, and alcohols is relatively increased. CI Solvent Violet 1 [6421-64-3] (**133**) (CI 12196), a 2:1 cobalt complex, illustrates this second type.



(**133**)

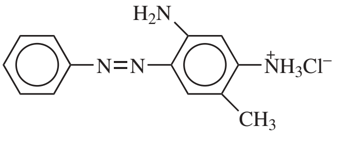
**5.7. Basic (Cationic) Azo Dyes.** Basic dyes of the azo class are the simplest and oldest known synthetic dyes. Earlier dyes, which were used for paper, leather, and in dyeing and printing of tanning-mordanted cotton, had poor to moderate lightfastness and washfastness. When polyacrylonitrile fibers were developed, these dyes gained importance because they showed superior lightfastness. Current cationic dyes are used for modified acrylics, modified nylons, modified polyesters, leather, unbleached papers, and inks. An important application is for conversion into pigments. Acrylics, nylon, and polyester fibers are modified by incorporation of acidic groups as dye sites in the fiber to increase its ability to be dyed with basic dyes. Principal chemical classes include azo, anthraquinone, triarylmethane, methine, thiazine, oxazine, etc (112). The dyes are applied in acidic dyebaths to fibers made of negatively charged polymer molecules.

Cationic azo dyes carry a positive charge in the chromophore portion of the molecule. The salt-forming counterion is usually a chloride or acetate. CI basic dyes are ammonium, sulfonium, or oxonium salts. Commercial basic azo dyes for which chemical structures are revealed by U.S. producers are listed in Table 15.

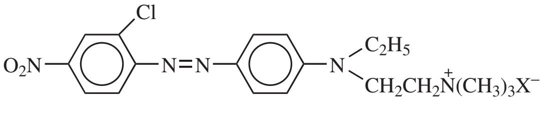
Basic Orange 1 (**134**) (aniline coupled to 2,4-diaminotoluene) and Basic Orange 2 (**22**) (aniline coupled to *m*-phenylenediamine) are examples of amine salt type cationic azo dyes. The cation is formed by protonation under acidic conditions. Under neutral or alkaline conditions, these dyes behave more like disperse dyes.

Table 15. **Commercial Basic Azo Dyes**

| CI name | Structure number | CAS Registry number | CI number |
|---|---|---|---|
| Basic Yellow 15 | | [72208-25-4] | 11087 |
| Basic Yellow 24 | | [52435-14-0] | 11480 |
| Basic Yellow 25 | (**140**) | [41025-67-6] | 11450 |
| Basic Yellow 57 | | [68391-31-1] | 12719 |
| Basic Orange 1 | (**134**) | [4438-16-8] | 11320 |
| Basic Orange 2 | (**22**) | [532-82-1] | 11270 |
| Basic Red 18 | (**135**) | [14097-03-1] | 11085 |
| Basic Red 22 | (**138**) | [12221-52-2] | 11055 |
| Basic Red 24 | | [37216-10-7] | 11088 |
| Basic Red 29 | (**139**) | [42373-04-6] | 11460 |
| Basic Red 39 | | [12221-63-5] | 11465 |
| Basic Red 76 | | [68391-30-0] | 12245 |
| Basic Blue 41 | (**137**) | [12270-13-2] | 11105 |
| Basic Blue 54 | (**136**) | [15000-59-6] | 11052 |
| Basic Blue 65 | | [12221-37-3] | 11076 |
| Basic Blue 66 | | [12221-38-4] | 11075 |
| Basic Blue 67 | | [12221-39-5] | 11185 |
| Basic Brown 1 | | [10114-58-6] | 21000 |
| Basic Brown 2 | | [6358-83-4] | 21030 |
| Basic Brown 4 | | [5421-66-9] | 21010 |
| Basic Brown 16 | | [26381-41-9] | 12250 |
| Basic Brown 17 | | [71134-97-9] | 12251 |
| Basic Black 2 | | [4443-99-6] | 11825 |



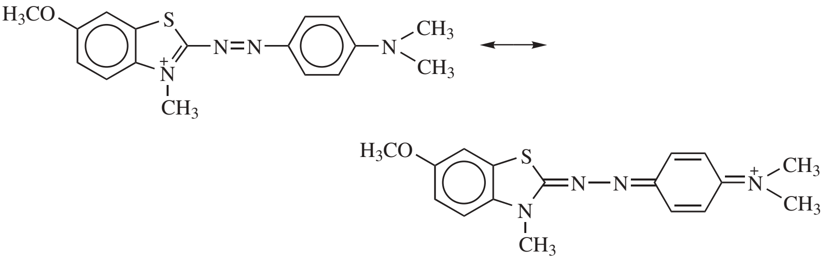
(**134**)



(**135**)

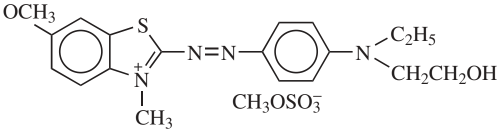
Basic Red 18 (**135**), Basacryl Red X-NL [14097-03-1] is an example of a pendant cationic azo dye, in which a localized positive charge is not conjugated with the chromophoric system. *N*-Ethyl-*N*-(2-chloroethyl)aniline [92-49-9] reacts with trimethylamine to form the ammonium salt coupler. The diazo component in Basic Red 18 is 2-chloro-4-nitroaniline [121-87-9].

So-called delocalized cationic azo dyes are another type in which the positive charge is delocalized (or distributed) across the dye cation. Basic Blue 54 (**136**) (2-amino-6-methoxybenzothiazole coupled to *N,N*-dimethylaniline and then quarternized with dimethyl sulfate) is an example of this class which can also be considered as a diazamethine dye.



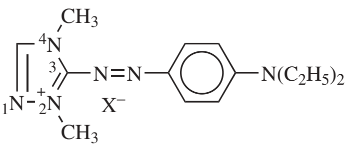
(**136**)

Another bright blue dye from diazotized 2-amino-6-methoxybenzothiazole [1747-60-0] by azo coupling, eg, with 2(*N*-ethylanilino)ethanol is Basacryl Blue X-3GL [12270-13-2] (**137**) (CI Basic Blue 41; CI 11105). After coupling, the water-insoluble dye is methylated at the thiazole nitrogen.

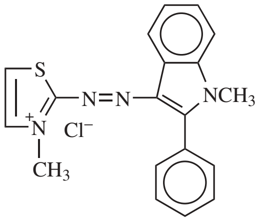


(**137**)

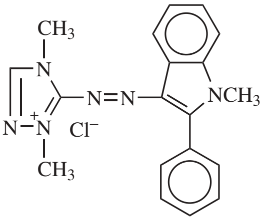
Basic Red 22 (**138**), which contains 1 part in 7 of the yellowish red 1,4-dimethyl isomer, Basic Red 29 (**139**), and Basic Yellow 25 (136) are all examples of delocalized cationic azo dyes. Dyes of this type can also be synthesized by Hünig's oxidative coupling reaction of heteroaromatic hydrazones with tertiary aromatic amines.



(**138**)



(**139**)

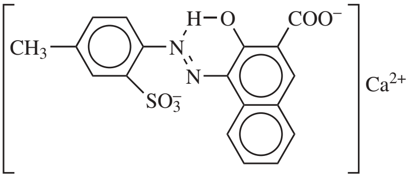


(**140**)

### 5.8. Azo Pigments.

Organic pigments are an important class of organic colorants. Expanding areas of usage include the mass coloration of synthetic fibers and textile printing in the textile field, and in the nontextile area, plastics. A pigment is insoluble in the medium in which it is used. The physical properties of pigments are of great significance since the coloring process does not involve solution of the colorant. Azo pigments can be grouped as metal toners, metal chelates, and metal-free azo pigments.

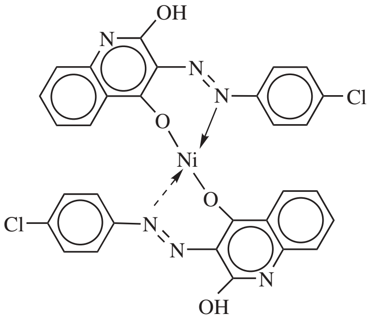
The first synthetic organic pigments were used to shade or tone the weaker colorants and became known as toners. Metal toners usually contain one sulfonic acid group and often a carboxylic acid group. The pigment is rendered insoluble, ie, *laked* with a heavy metal cation. An example of a calcium salt is Lithol Rubine BK [5858-81-1] (**141**) (CI Pigment Red 57; CI 15850).



(**141**)

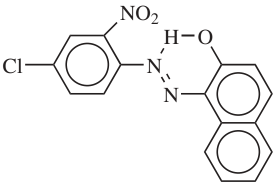
Toners derived from 6-chlorometanilic acid [88-43-7], 6-amino-4-chloro-*m*-toluene-sulfonic acid [88-51-7], and 6-amino-*m*-toluenesulfonic acid [88-44-8] have improved fastness properties and find use in paints, inks, and plastics.

Metal chelation is also a means of insolubilizing organic molecules. For example, CI Pigment Green 10 [51931-46-5], (**142**) (CI 12775) is a 2:1 nickel complex of a bidentate *o*-hydroxyazo ligand.

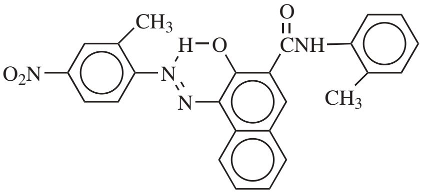


(**142**)

In the metal-free class of azo pigments it is remarkable that the simplest derivatives of 2-naphthol such as Hansa Red B [2425-85-6] (**143**) (CI Pigment Red 3; CI 12120, Toluidine Red) and Para Red [6410-10-2], both known since 1905, are still of importance.



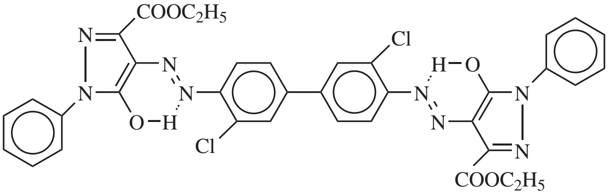
(**143**)



(**144**)

Because these pigments are organic in nature they tend to bleed in resins and solvents. Increasing the molecular weight often reduces this tendency. For this reason, I.G. Farbenindustrie introduced a line of pigments based on Naphthol AS as the coupling component, eg, Permanent Bordeaux FRR Extra [6410-32-8] (**144**) (CI Pigment Red 12; CI 12385).

In the same way acetoacetanilides and pyrazolones can be used as coupling components. Larger molecules can be formed in the pigment series by using a benzidine derivative as the middle component as, eg, in Vulcan Fast Red B [6358-87-8] (**145**) (CI Pigment Red 38; CI 21120).



(**145**)

A survey of organic pigments has been done (113). A more recent publication on organic pigments (114), describes their syntheses, chemical and physical properties, and the technology of the various applications.

## 6. Economic Aspects

In 1998 global consumption of dyes dropped almost 15% due to financial problems in Asia and changes in the fashion industry. In 1999, production/consumption declined by 10% compared to 1998. Consumption of dyes is governed by the demand for textiles, leather, and colored paper (115).

India, the former USSR, Eastern Europe, China, the Republic of Korea, and Taiwan consumed $600 \times 10^3$ t/yr. Western Europe, the United States, and Japan consume more textiles at a higher rate than growing countries. The rate in India and other developing countries is growing at a fast rate, however.

Migration of the world apparel and textile industries to growing countries will impact the consumption figures. China is the leading producer of dyes ($200 \times 10^3$ t/yr).

Environmental laws covering air, water, and waste emissions are the largest concerns for the dye industry. The U.S. Toxic Substances Control Act has made development of new dyes costly. Western Europe and Japan have similar problems. Pollution abatement costs are rising in these countries and is a growing concern in other countries, such as China, as well.

Table 16. **Safety Profiles for Some Azo Dyes**[a]

| Dye | Safety profile |
|---|---|
| Acid Blue 41 | eye irritant |
| Acid Blue 62 | moderately toxic by intraperitoneal route, mutation data reported |
| Acid Blue 129 | skin and eye irritant |
| Acid Blue 185 | moderately toxic by intraperitoneal route, low toxicity by ingestion |
| Acid Green 40 | mildly toxic by ingestion, eye irritant |
| Acid Red 98 | mutation data reported |
| Acid Violet 7 | low toxicity by ingestion |
| Acid Yellow 3 | low toxicity by ingestion |
| Acid Yellow 7 | poison by intravenous route |
| Basic Orange 1 | mutation data reported |
| Basic Orange 21 | moderately toxic by ingestion |
| Basic Red 13 | moderately toxic by ingestion |
| Basic Red 29 | mutation data reported |
| Direct Blue 2 | low toxicity by ingestion, eye irritant<br>mutation data reported |
| Direct Blue 218 | moderately toxic by ingestion, low toxicity by skin contact, mutation data reported |
| Direct Brown 31 | mutation data reported |
| Direct Red 39 | mutation data reported |
| Direct Red 81 | moderately toxic by interperitoneal route, mutation data reported |
| Direct Green 1 | mutation data reported |
| Disperseb Blue 27 | mutation data reported |
| Disperse Red 29 | mutation data reported |
| Disperse Yellow 7 | moderately toxic by unspecified route |

[a] From Ref. 117.

The European Community has added two new azo dyes to the banned list. (*o*-anisidine and 4-aminobenzene). Products must be free of these amines to be exported to the EU. All products made of textiles and leather (if they come in direct contact with human skin and oral cavity) are covered in this directive (116).

## 7. Health and Safety Factors

Safety profiles for some representative dyes are listed in Table 16. All of the dyes listed here emit toxic vapors when heated to decomposition.

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RASIK J. CHUDGAR
BASF Corporation

JOHN OAKES
John Oakes Associates