Manufacture of Dye Intermediates, Dyes, and Their Industrial Applications

R.W. Sabnis

Abstract

Synthesis of industrially important dye intermediates and dyes is presented. Industrial applications of dyes including textiles and non-textiles such as acid-base indicators, liquid crystal, color filters for displays and sensors, ink-jet, lasers, photographic, hairs, food, and biomedical are discussed.

Keywords

Dye intermediates • Dyes • Dyeing • Manufacture • Industrial Applications

Introduction

Synthesis of industrially important dye intermediates and dyes is presented. Industrial applications of dyes including textiles and non-textiles such as acid-base indicators, liquid crystal, color filters for displays and sensors, ink-jet, lasers, photographic, hairs, food, and biomedical are discussed.

Manufacture of Dye Intermediates

This section provides an overview of the chemical reactions used in preparing the key intermediates employed in dye synthesis. The term “intermediates” refers to those compounds, which are prepared from the original coal tar constituents by various chemical reactions and which, in turn, can be converted into commercial dyes by relatively simple further transformations. A typical example is aniline, which is synthesized from benzene by various methods and can be converted into a wide variety of dyes. Thus, the raw materials used to synthesize organic dyes are commonly referred to as “dye intermediates.” Most of the intermediates entering into the preparation of commercial synthetic organic dyes are members of the aromatic series, which are mainly derivatives of benzene, naphthalene, and anthraquinone [1, 2].

There are three types of reactions involving substitution of the hydrogen atoms of the benzene nucleus, which differ in the nature of

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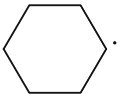
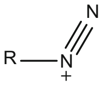
attacking reagent. The three types of attacking reagents are (1) electrophilic reagents (electron accepting or electron loving); (2) nucleophilic reagents (electron donating or nucleus loving); and (3) free radical reagents as given in Table 1.

Mechanism of Electrophilic Reagents

The electrophilic reagent is deficient in electrons, which reacts with the aromatic nucleus at a point of high electron density and establishes a bond by sharing an electron pair. After the initial fusion of the attacking group to the activated aromatic nucleus, the reaction is completed by the discharge of a proton and a return of the molecule from an unstable intermediate to a stable compound as shown in Scheme 1. The greater majority of the familiar reactions involving direct substitution on the aromatic hydrocarbon fall into this category.

Table 1 Attacking reagents

Electrophilic reagents	Nucleophilic reagents	Free radical reagents
Cl^+	–OH	$F^{\bullet}$
Br^+	$-OCH_3$	$Cl^{\bullet}$
$NO_2{}^+$	$-NR_2$	
SO_3H^+	–SR	
	–CN	

R = H or alkyl

Mechanism of Nucleophilic Reagents

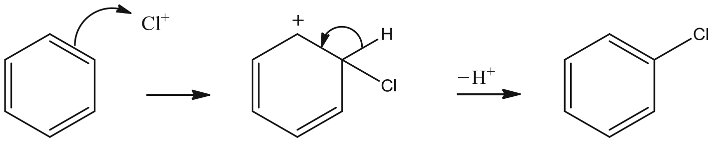
The nucleophilic reagent possesses an unshared electron pair. In nucleophilic substitution reaction, hydrogen is seldom replaced. The replaced groups are ordinarily halogen atoms or other groups possessing reasonable stability as anions. The nucleophilic reagent may be either a charged particle or a neutral molecule, e.g., ammonia. The nucleophilic reagent attacks the aromatic system at a point of low electron density corresponding to positions which are unreactive to the more familiar electrophilic reagent. The nucleophilic substitution reactions involve replacement of groups which are activated through other substituents in the aromatic nucleus. Thus, the nitro group in the following example directs the attacking nucleophilic group (:OH) to the ortho position as shown in Scheme 2.

Most dye intermediates are prepared by reactions involving either electrophilic or nucleophilic substitution reactions.

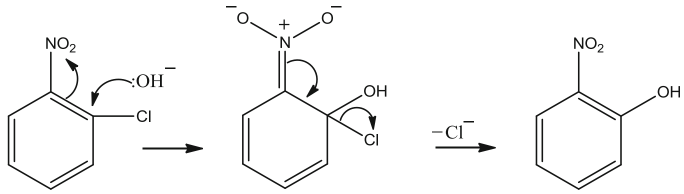
Orientation Rules and Effects

The dye chemist is frequently faced with challenges of preparing new intermediates having a prescribed constitution and location of

Scheme 1 Mechanism of electrophilic reagents



Scheme 2 Mechanism of nucleophilic reagents



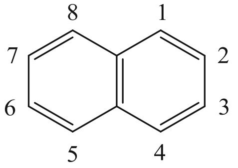
substituents. The solution to this challenge is made much easier by an accurate knowledge of all of the laws governing the positions taken by substituents, when they are introduced into the various aromatic ring systems.

Orientations in the Benzene Nucleus

The directing or orienting influence of the substituents can be divided into two classes. Class 1 includes alkyl, aryl (diphenyl), halogen, –OH, –OR, –O-acyl, $-NH_2$, –NHR, NR_2, –NH-acyl, –NR-acyl, and –N=N–. These groups direct an incoming substituent exclusively or nearly so to the ortho and para positions. Class 2 includes $-NO_2$, $-SO_3H$, $-SO_2Cl$, $-SO_2R$, –COOH, –COOR, –CONHR, –COR, –CHO, and –CN. These groups orient predominately, but seldom exclusively, to the meta position.Whether the ortho or para position is favored by the Class 1 substituents depends partly on the particular substituent present, but also to a large degree on the nature of the entering group and often on the reaction conditions, especially the temperature. The directing influence of primary, secondary, and tertiary amino groups is significantly reduced by the presence of large quantities of concentrated sulfuric acid. If there are already two substituents in the benzene ring, they may either direct the third entering group to the same position or work in opposition to each other. When substituents of the two classes are working in opposition, the influence of Class 1 groups usually predominates or completely masks the influence of the Class 2 groups.

Orientations in the Naphthalene Nucleus

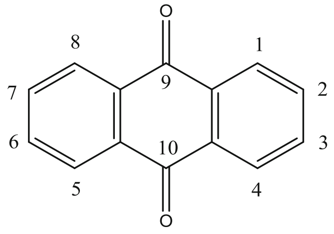
The chemical structure and numbering of the naphthalene are given below



In the naphthalene series, two isomers, namely, α-isomer and β-isomer, are possible when only one substituent is present. Nitration and halogenation of naphthalene give only the α-compound. On the other hand, sulfonation with concentrated sulfuric acid always gives a mixture of two isomers; the relative amounts of the two depend on the sulfonation temperature. In cold, the chief product is α-sulfonic acid, while at temperatures above 120–130 °C, the β-sulfonic acid predominates.Groups of Class 1, which are strongly orienting (alkoxy, hydroxyl, amino, or acylamino groups in the absence of concentrated sulfuric acid), when present in the 1 position of the naphthalene nucleus, direct the entering substituent in ortho or para position (2 and 4 positions) similar to benzene nucleus. Groups of Class 1, which are less active (halogen and amino groups in the presence of concentrated sulfuric acid), when present in the 1 position of the naphthalene nucleus, often produce 5 isomer, instead of the 2 isomer, along with the 4-substituted compound. Groups of Class 1, when present in the 2 position of the naphthalene nucleus, direct partly to 1 position and partly to the positions in the other ring, especially the 8 position and then the 6 position. Groups of Class 2 favor the entrance of a second substituent into the other ring almost exclusively; the meta position of the same ring is usually entered only if there are other substituents already present in the other ring.

Orientations in the Anthraquinone Nucleus

The chemical structure and numbering of the anthraquinone are given below



In the anthraquinone series, the orientation is different from benzene and naphthalene. In contrast to benzene and naphthalene, anthraquinone is not easily sulfonated with concentrated sulfuric acid because the temperature is so high that the anthraquinone structure is destroyed. When anthraquinone is sulfonated with fuming sulfuric acid, the sulfo group enters almost exclusively in 2-position (β-position). If sulfonation is carried out in the presence of mercury salts, the first sulfo enters in 1-position (α-position) preferentially. If the sulfonation is further carried out, at least four isomers, 1,5-, 1,6-, 1,7-, and 1,8-isomers, are obtained. Nitration of anthraquinone proceeds in a manner analogous to sulfonation, except that the mercury salts have no effects on the orientation. Amination of anthraquinone is achieved either by replacing sulfo group by $-NH_2$ group or by reducing nitro group. Halogenation of anthraquinone takes place only with difficulty but the hydroxyl and amino derivatives can be easily halogenated, particularly with bromine.

Fundamental Processes in Dye Chemistry

The modern dye industry is built upon the coal tar industry as its source of material and upon the Kekule benzene theory as its scientific basis. In this section, fundamental processes involved in dye chemistry are discussed. The fundamental processes include sulfonation, nitration, reduction, amination, hydroxylation, oxidation, halogenation, and diazotization/coupling.

Sulfonation

The introduction of a sulfonic acid group (s) ($-SO_3H$) into a molecule is called sulfonation. Sulfonation is of the greatest importance in dye manufacture. Most of the water-soluble dyes owe their solubility to the presence of sulfonic acid groups. In addition, sulfonic acids are extremely important intermediates in the presence of phenols, especially in the naphthalene series. Sulfonation is carried out by using (1) concentrated sulfuric acid; (2) a combination of concentrated sulfuric acid and fuming sulfuric acid (sulfur trioxide (SO_3)) (oleum); (3) sulfur trioxide in an inert solvent such as 1,2-dichloroethane or sulfur dioxide; (4) sulfur trioxide with ether or an organic base (pyridine); or (5) chlorosulfonic acid.

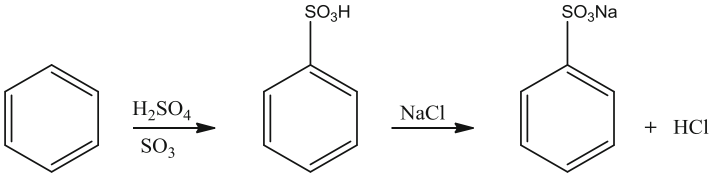
Sulfonic acid group can also be introduced (1) by replacing a halogen atom with the sulfonic acid group by means of sodium sulfite; (2) by the action of bisulfite on a nitro compound or on a quinone compound; (3) by oxidation of a disulfide, a mercaptan, or a sulfinic acid; or (4) by the introduction of the $-CH_2SO_3H$ group by means of formaldehyde-bisulfite [3–5].

Sulfonation of Benzene

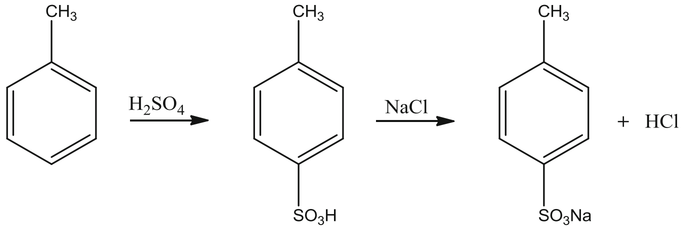
Benzene can be monosulfonated using excess of concentrated sulfuric acid; however, better results are obtained using oleum (7–8% SO_3). Because of the high solubility of sulfonic acids in water, they are usually not isolated from aqueous solution in the free state, but are converted into and isolated as their sodium salts as given in Scheme 3.

Sulfonation of Toluene

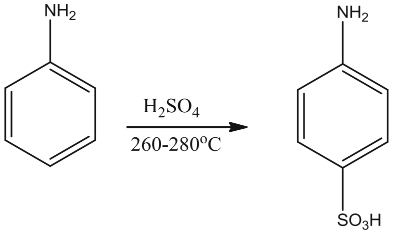
The sulfonation of toluene with concentrated sulfuric acid at 100–120 °C results in the formation of toluene-p-sulfonic acid as the main product, accompanied by small amounts of the ortho and meta isomers, which can be easily removed by crystallization of the sodium salt of the para isomer in the presence of sodium chloride as shown in Scheme 4.



Scheme 3 Sulfonation of benzene



Scheme 4 Sulfonation of toluene



Scheme 5 Sulfonation of aniline

Sulfonation of Aniline

Aromatic aminosulfonic acids constitute an important class of dye intermediates particularly for azo dye chemistry. Aromatic amines are sulfonated by two methods: (1) direct and (2) indirect or baking process. The direct procedure is carried out at a comparatively low temperature with concentrated sulfuric acid or a combination of sulfuric acid and dissolved sulfur trioxide (oleum). The indirect or baking process involves a high-temperature baking of amine and sulfate. The indirect or baking process offers the advantage of giving products more nearly free of isomers and favors substitution in the para position when both ortho and para positions are available in the aromatic nucleus. Aniline is sulfonated by indirect or baking process using concentrated sulfuric acid at 260–280 °C giving aniline-4-sulfonic acid (sulfanilic acid) in 94.5% yield as shown in Scheme 5.

Sulfonation of Naphthalene

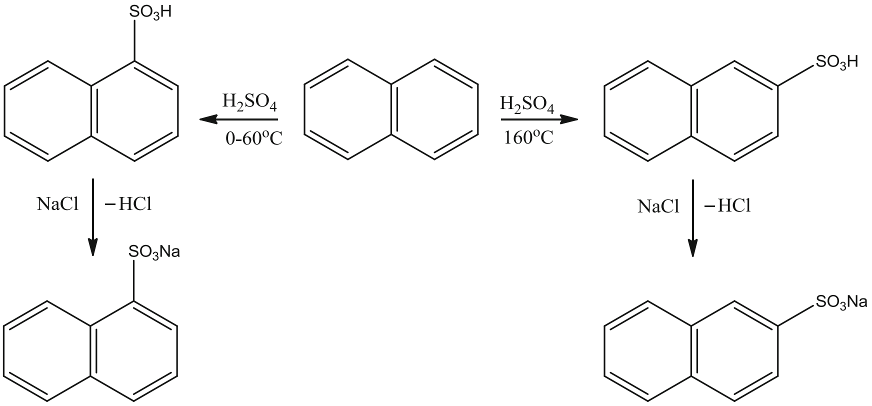
Sulfonation of naphthalene with concentrated sulfuric acid at lower temperatures (0–60 °C), often below 30 °C, almost exclusively gives naphthalene-1-sulfonic acid (the product of kinetic control), whereas sulfonation of naphthalene with concentrated sulfuric acid at about 160 °C for about 2 h yields largely naphthalene 2-sulfonic acid (the product of thermodynamic control). In both cases, the product is isolated as sodium salt as shown in Scheme 6.

Sulfonation of β-Naphthol

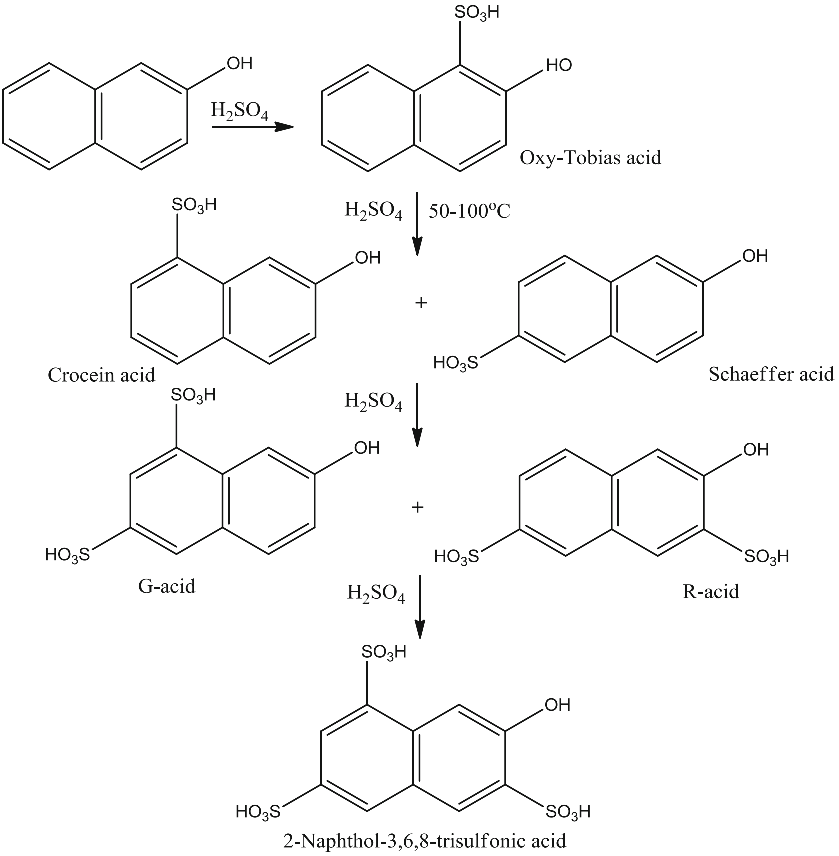
Sulfonation of β-naphthol presents a more complex picture in which the temperature, concentration, amount of sulfonating agent, and duration of the reaction all affect the identity and yield of the products. β-Naphthol with concentrated sulfuric acid at room temperature or under ice-cold conditions affords 2-naphthol-1-sulfonic acid (Oxy-Tobias acid), which on further treatment with concentrated sulfuric acid at 50–100 °C yields a mixture of 2-naphthol-8-sulfonic acid (crocein acid) and 2-naphthol-6-sulfonic acid (Schaeffer acid). Increasing the temperature gives increasing amounts of 2-naphthol-8-sulfonic acid (crocein acid), while at higher temperatures, 2-naphthol-6-sulfonic acid (Schaeffer acid) predominates. Increasing the acid concentration produces 2-naphthol-6, 8-disulfonic acid (G acid) and 2-naphthol-3, 6-disulfonic acid (R acid), which are very important azo dye intermediates, and finally 2-naphthol-3,6,8-trisulfonic acid as shown in Scheme 7.

Sulfonation of Anthraquinone

The sulfonation of anthraquinone in the presence of mercury salts and oleum gave anthraquinone-1-sulfonic acid. Further sulfonation of 1-monosulfonic acid in the presence of mercury salts and oleum gave anthraquinone-1,5-disulfonic acid and anthraquinone-1,8-disulfonic acid. In both cases, the product is isolated as sodium salt as shown in Scheme 8.



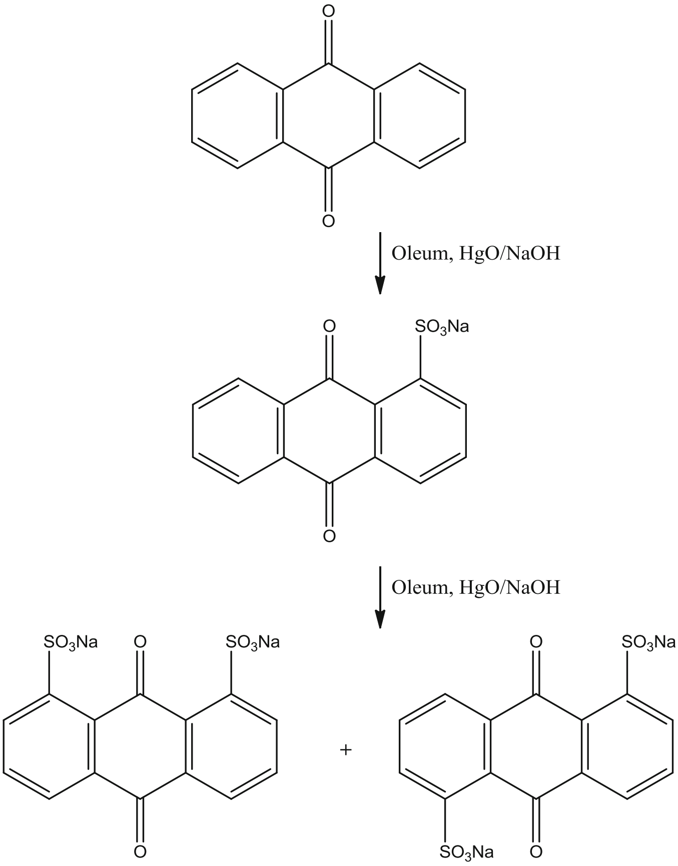
Scheme 6 Sulfonation of naphthalene



Scheme 7 Sulfonation of β-naphthol

The carbonyl groups in anthraquinone deactivate the aromatic nucleus towards electrophilic attack and vigorous conditions for sulfonation such as oleum at about 160 °C are required. The product is largely anthraquinone-2-sulfonic acid. Further sulfonation of 2-monosulfonic acid in the presence of mercury salts and oleum gave anthraquinone-2,6-disulfonic acid and anthraquinone-2,7-disulfonic acid. In both cases, the product is isolated as sodium salt as shown in Scheme 9.

Scheme 8 Sulfonation of anthraquinone



Nitration

The process of nitrating the benzene nucleus is one of the most important processes since the resulting nitro compounds can be readily reduced to the corresponding amines, which have broad applications in dye chemistry. Nitration process involves the introduction of one or more nitro groups (NO_2) into the aromatic nucleus. Nitric acid (HNO_3) in both aqueous and organic solvent systems can be used for nitrating more reactive compounds, whereas less reactive compounds require a combination of nitric acid (HNO_3) and sulfuric acid (H_2SO_4), which is called as mixed acids. The sulfuric acid serves as a solvent for carrying out the reaction. In addition, it is effective in reacting with nitric acid molecule to form the nitronium ion (NO_2^+), which is the actual nitrating agent [3–5]. The representative examples of nitration reactions are given below.

Nitration of Benzene

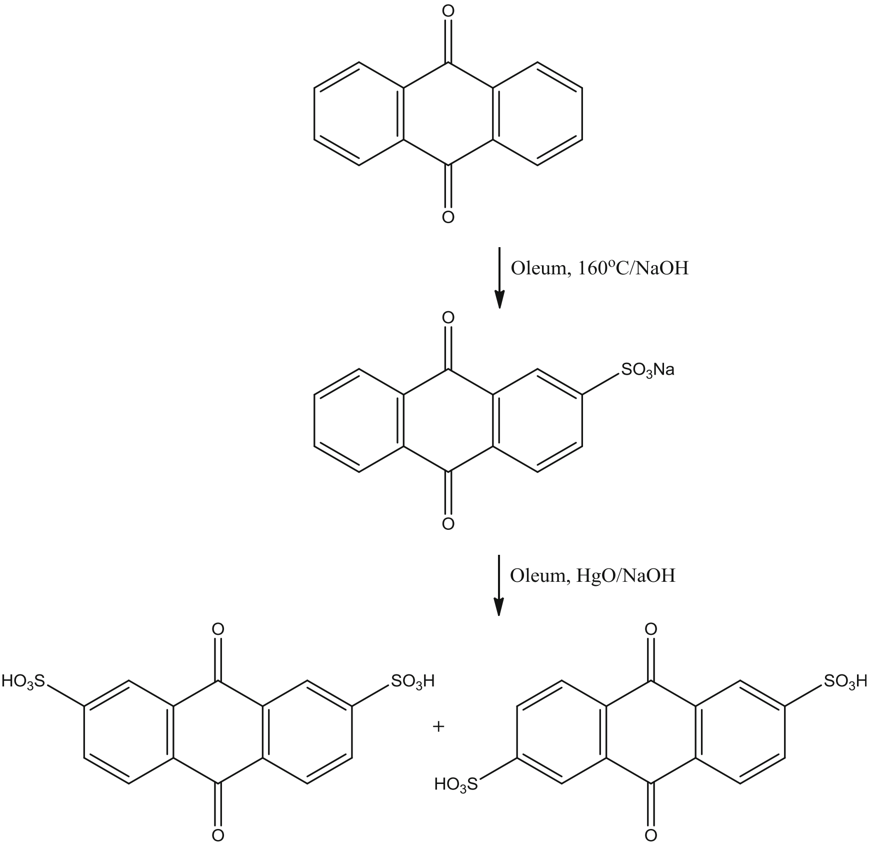
Benzene is nitrated with concentrated nitric acid and concentrated sulfuric acid yielded nitrobenzene as shown in Scheme 10.

Nitration of Toluene

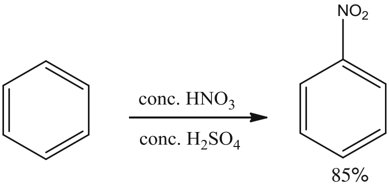
When toluene is nitrated with concentrated nitric acid and concentrated sulfuric acid, a mixture of o-, p-, and m-nitrotoluene is obtained in 63%, 35%, and 2%, respectively, as shown in Scheme 11.

Nitration of Phenol

Phenol can be converted into a mixture of 2- and 4-nitrophenols by reaction with dilute nitric acid



Scheme 9 Sulfonation of anthraquinone



Scheme 10 Nitration of benzene

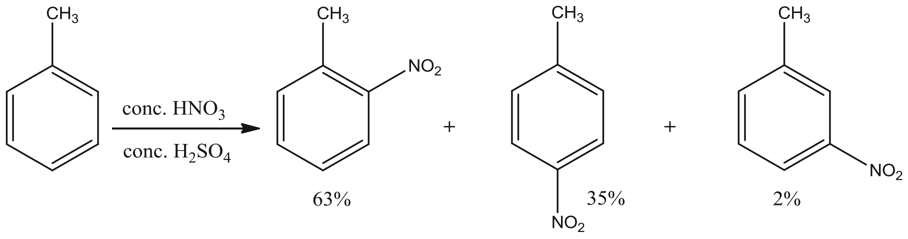
as shown in Scheme 12. The yield of 4-nitrophenol can be increased if a mixture of sodium nitrate and dilute sulfuric acid is employed.

Nitration of Naphthalene

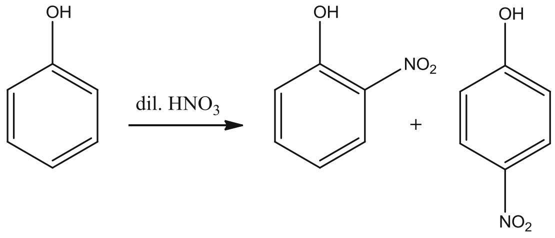
Nitration of naphthalene proceeds readily by using mixed acids of lower concentration than in the case of benzene at 50–60 °C giving almost exclusively 1-nitronaphthalene in 95% yield and 2-nitronaphthalene in 5% yield. Further nitration gives first a mixture of 1,5- and 1,8-dinitronaphthalene and next principally, 1,4,5- and 1,3,8-trinitronaphthalene as shown in Scheme 13.

Nitration of 1-Naphthol and 2-Naphthol

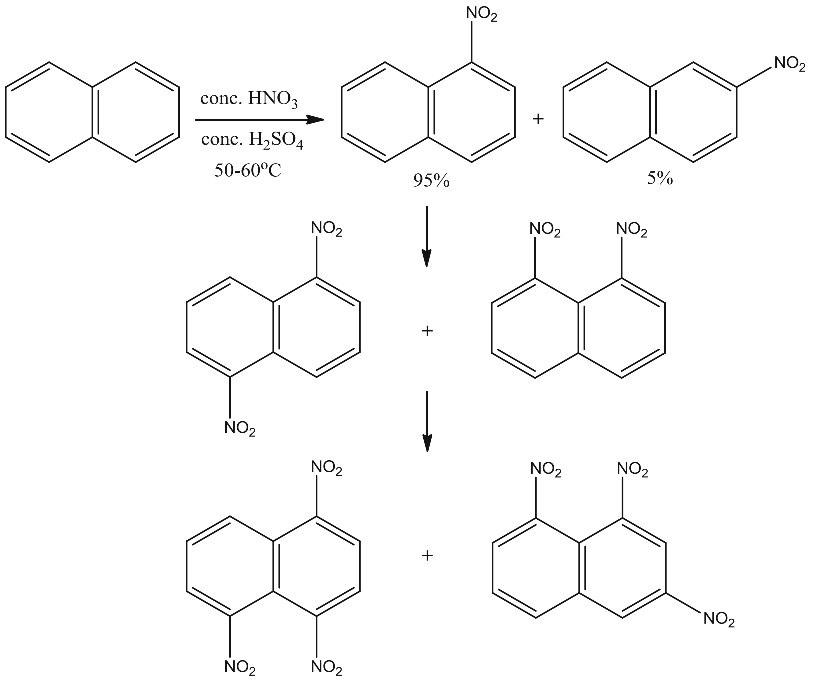
The hydroxyl group of 1-naphthol directs nitro group into the 2- and 4-positions. Thus, nitration of 1-naphthol gave 2,4-dinitro-1-naphthol as shown in Scheme 14, while nitration of 2-naphthol in the cold in the presence of mercuric nitrate afforded good yield of 1-nitro-2-naphthol as shown in Scheme 15.



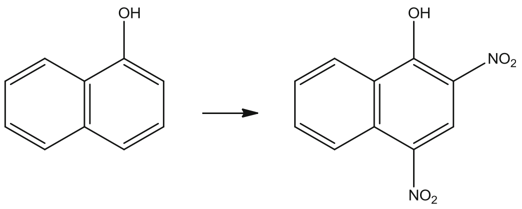
Scheme 11 Nitration of toluene



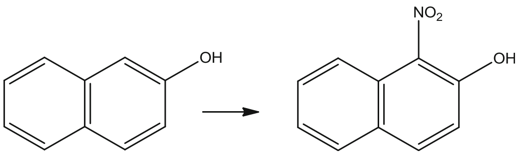
Scheme 12 Nitration of phenol



Scheme 13 Nitration of naphthalene



Scheme 14 Nitration of 1-naphthol



Scheme 15 Nitration of 2-naphthol

Nitration of 1-Naphthylamine and 2-Naphthylamine

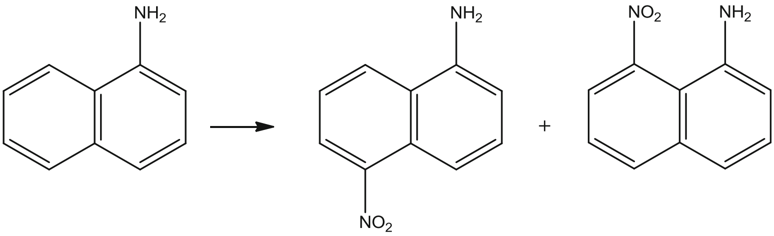
1-Naphthylamine cannot be nitrated at the ordinary temperature without some decomposition. 1-Naphthylamine can be nitrated with nitric acid in a large excess of sulfuric acid below 0 °C yielding mainly the 5-nitro-1-naphthylamine and 8-nitro-1-naphthylamine as shown in Scheme 16. Similarly, 2-naphthylamine when nitrated with sulfuric acid gives mainly the 5-nitro-2-naphthylamine and 8-nitro-2-naphthylamine as shown in Scheme 17.

Nitration of Anthraquinone

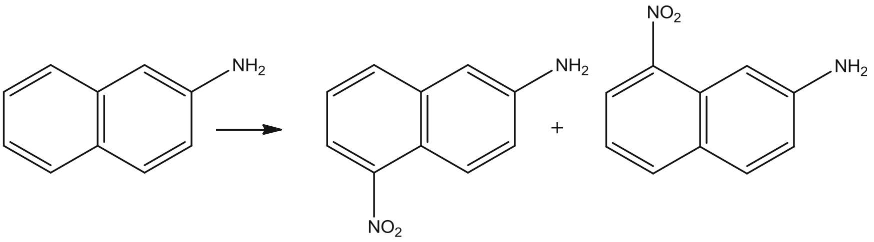
The nitration of anthraquinone requires rather more drastic conditions than in the case of naphthalene or benzene. Since the reactivities of the two benzene rings in the anthraquinone molecule are largely independent of each other, exclusive mononitration is not possible. Anthraquinone undergoes nitration with sulfuric acid and nitric acid at about 80 °C, when 1,5-dinitroanthraquinone begins to separate, and the mixture is further heated at 125 °C for 2 h, when the separated yellow precipitate of 1,5-dinitroanthraquinone is filtered. The acid mother liquor contains 1,8-, 1,6-, and 1,7-dinitroanthraquinones, which have no technical value. Nitration of anthraquinone is given in Scheme 18.

Reduction

Most frequently encountered reduction by the dye chemist is the transformation of a nitro compound into an amino compound. However, there are several other reduction methods, which play

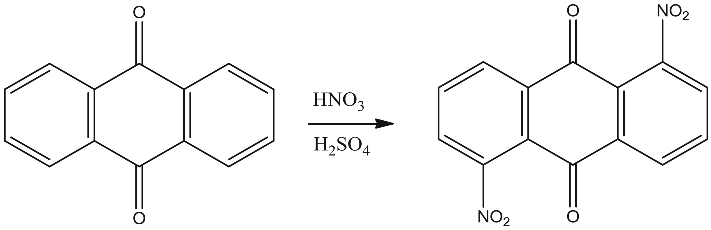


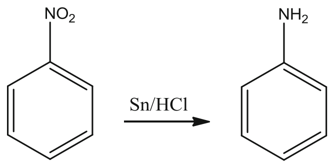
Scheme 16 Nitration of 1-naphthylamine



Scheme 17 Nitration of 2-naphthylamine

Scheme 18 Nitration of anthraquinone





Scheme 19 Reduction of nitrobenzene

a vital role in dye chemistry. This section covers the reduction of nitro and azo compounds into amino compounds. Some of the reducing agents employed are summarized below: (1) reduction with iron, water, and addition of a small amount of acid; (2) reduction with iron and addition of enough (a large amount of) acid; (3) reduction with zinc dust and acid or alkali; (4) reduction with ferrous hydroxide $Fe(OH)_2$; (5) reduction with hydrogen sulfide and its salts; (6) reduction with hydrosulfite; (7) reduction with sulfur dioxide; (8) reduction with aluminum powder; (9) catalytic reduction with hydrogen; and (10) electrolytic reduction. In addition to the above-mentioned reducing agents, there are a wide variety of reducing agents [3–5].

Reduction of Nitrobenzene

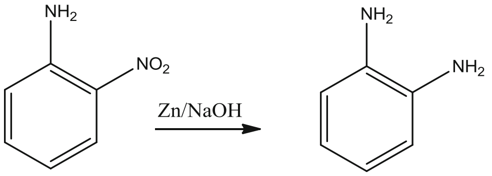
For example, nitrobenzene reduced with tin and hydrochloric acid gave aniline as shown in Scheme 19.

Reduction of o-Nitroaniline

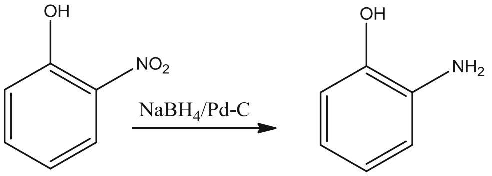
Compounds which are sensitive to acidic conditions may sometimes be successfully reduced to amines under alkaline condition. o-Nitroaniline reduced with zinc and sodium hydroxide gave o-phenylenediamine as shown in Scheme 20, which is an important key intermediate in dye chemistry.

Reduction of o-Nitrophenol

o-Nitrophenol can be readily reduced in good yield to o-aminophenol by sodium borohydride in aqueous methanol solution in the presence of a palladium-on-carbon catalyst as shown in Scheme 21.



Scheme 20 Reduction of o-nitroaniline



Scheme 21 Reduction of o-nitrophenol

Reduction of 1-Nitronaphthalene

A catalytic process for the reduction of 1-nitronaphthalene using hydrogen in the presence of nickel catalyst gave 1-naphthylamine as shown in Scheme 22.

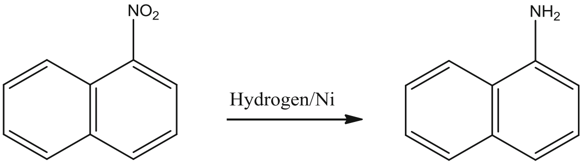
Reduction of 1-Phenylazo-2-naphthol and Methyl Orange

It is interesting to note that azo compounds can be conveniently reduced either by tin (II) chloride ($SnCl_2$) in hydrochloric acid or sodium dithionite. Thus, 1-phenylazo-2-naphthol is reduced to aniline and 1-amino-2-naphthol as shown in Scheme 23. Similarly, Methyl Orange is reduced to p-amino-N,N-dimethylaniline and sulfanilic acid as shown in Scheme 24.

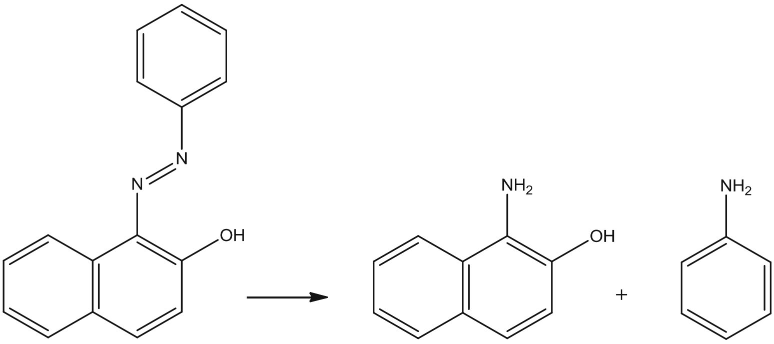
Reduction of 1-Nitroanthraquinone

1-Nitroanthraquinone reduced with boiling sodium sulfide solution gave 1-aminoanthraquinone as shown in Scheme 25.

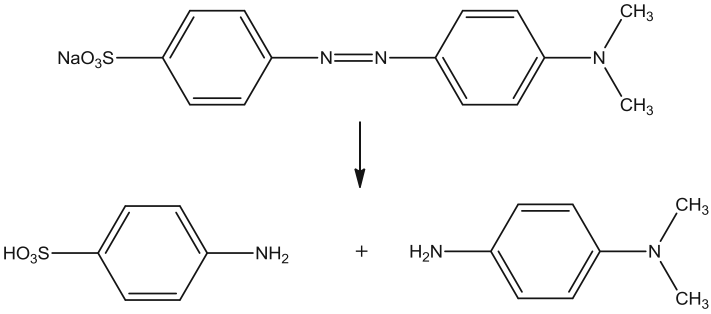
Scheme 22 Reduction of 1-nitronaphthalene



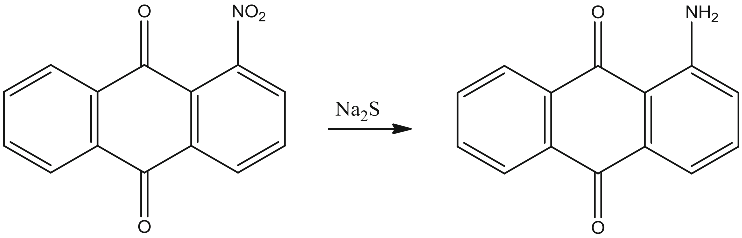
Scheme 23 Reduction of 1-phenylazo-2-naphthol



Scheme 24 Reduction of Methyl Orange



Scheme 25 Reduction of 1-nitroanthraquinone



Amination

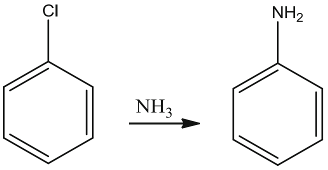
This section covers the replacement of a halogen by an amino group or the replacement of a phenolic hydroxyl group by an amino group [3–5].

Amination of Chlorobenzene

Aniline is prepared from chlorobenzene by treatment with sodamide in liquid ammonia as shown in Scheme 26. The reaction proceeds under vigorous conditions.

Amination of 2-Naphthol

Naphthalene intermediates containing amino groups can also be prepared by the replacement of a hydroxyl group with an amino group (Bucherer reaction). Thus, 2-naphthol is readily converted into 2-naphthylamine by heating with ammonium sulfite or ammonia at 150 °C in an autoclave as shown in Scheme 27.

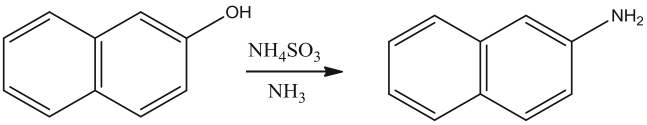


Scheme 26 Amination of chlorobenzene

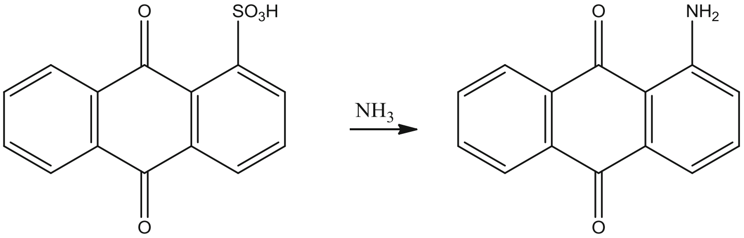
Amination of Anthraquinone-1-sulfonic acid, Anthraquinone-2-sulfonic acid, 2-Chloroanthraquinone and 2,3-Dichloroanthraquinone

Anthraquinone-1-sulfonic acid is converted into 1-aminoanthraquinone by reacting with ammonia and arsenic pentoxide at 180 °C as shown in Scheme 28. Similarly, 2-aminoanthraquinone is prepared from anthraquinone-2-sulfonic acid using ammonia and sodium arsenate as shown in Scheme 29. 2-Chloroanthraquinone upon heating with ammonia and arsenic acid in an autoclave gave 2-aminoanthraquinone as shown in Scheme 30. 2,3-Diaminoanthraquinone, an important intermediate in dye chemistry, is

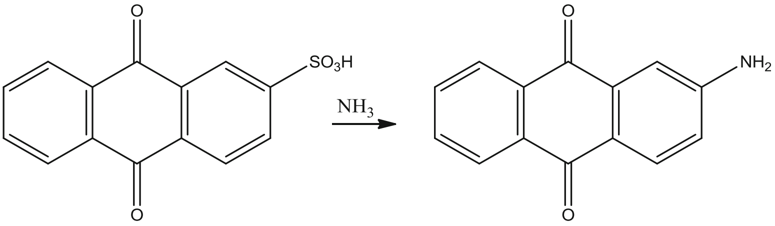
Scheme 27 Amination of 2-naphthol



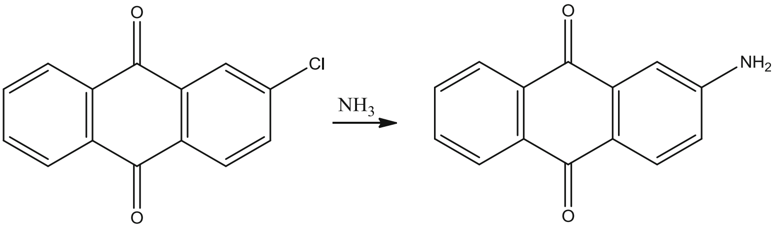
Scheme 28 Amination of anthraquinone-1-sulfonic acid

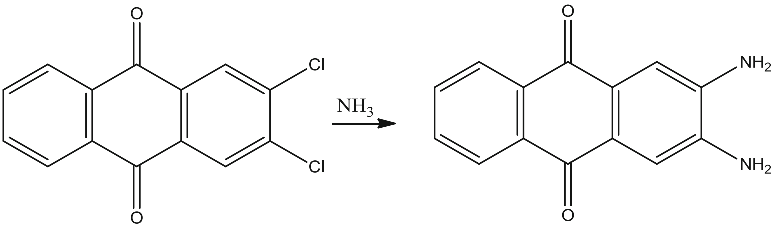


Scheme 29 Amination of anthraquinone-2-sulfonic acid

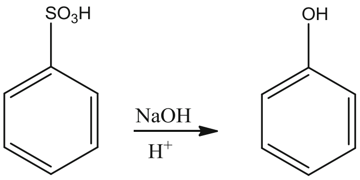


Scheme 30 Amination of 2-chloroanthraquinone





Scheme 31 Amination of 2,3-dichloroanthraquinone



Scheme 32 Hydroxylation of benzenesulfonic acid

synthesized by amination of 2,3-dichloroanthraquinone with ammonia as shown in Scheme 31.

Hydroxylation

The introduction of a hydroxyl group(s) (–OH) into a molecule is called hydroxylation. It is carried out by several methods such as (1) replacement of a sulfonic acid group by the hydroxyl group, via fusion of a sulfonic acid with alkali, e.g., sodium hydroxide or potassium hydroxide. When potassium hydroxide is used, the process is called "potash fusion"; (2) replacement of a labile halogen by the hydroxyl group; (3) replacement of a diazo group by the hydroxyl group; (4) heating an amine with acid or alkali under pressure [3–5].

Hydroxylation of Benzenesulfonic acid and Naphthalene-2-sulfonic acid

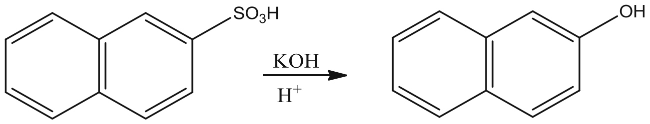
Alkali fusion that involves heating benzenesulfonic acid with either sodium hydroxide or potassium hydroxide in the presence of small amount of water to aid the fusion process gave phenol as shown in Scheme 32. Similarly, 2-naphthol is synthesized from naphthalene-2-sulfonic acid by alkali fusion with potassium hydroxide as shown in Scheme 33.

Hydroxylation of Anthraquinone-2-sulfonic acid

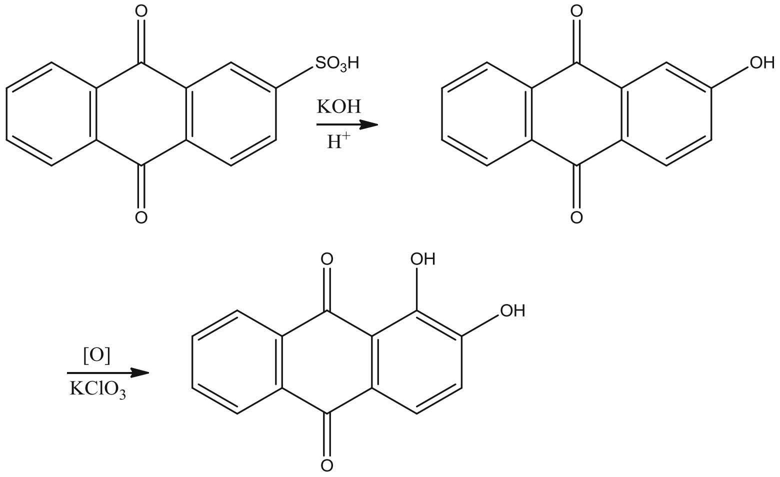
When sulfonic acid group is replaced by the hydroxyl group in the hydroxylation process, the oxidation products are occasionally formed. A particular example is the alkali fusion of anthraquinone-2-sulfonic acid, which results in 2-hydroxyanthraquinone, where the oxidation step is promoted by the deliberate introduction of potassium chlorate as an oxidant, where second hydroxyl group is introduced at 1-position forming the dyestuff, alizarin, as shown in Scheme 34.

Hydroxylation of 1-Chloro-4-nitrobenzene and 1-Chloro-2,4-dinitrobenzene

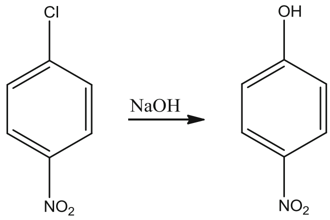
Direct nucleophilic displacement of the halogen in an aryl halide is difficult and the hydrolysis to phenols requires high temperatures and pressures. However, the presence of a nitro group in the *ortho* or *para* position makes the halogen more labile since electron withdrawal by the nitro groups in these positions stabilizes the intermediate anion by electron delocalization. For example, when 1-chloro-4-nitrobenzene was heated with 15% sodium hydroxide solution at about 150 °C, it gave 4-nitrophenol as shown in Scheme 35. When two activating nitro groups are present in *ortho* or *para* position, 1-chloro-2,4-dinitrobenzene is readily converted into 2,4-dinitrophenol as shown in Scheme 36.



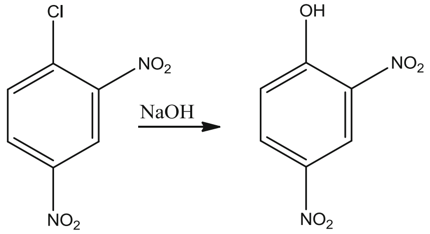
Scheme 33 Hydroxylation of naphthalene-2-sulfonic acid



Scheme 34 Hydroxylation of anthraquinone-2-sulfonic acid



Scheme 35 Hydroxylation of 1-chloro-4-nitrobenzene



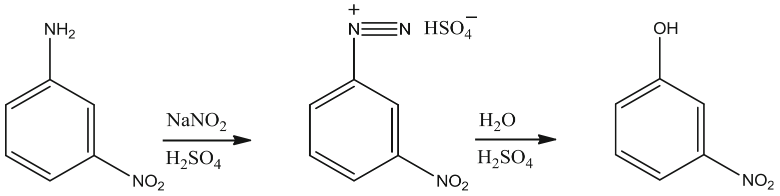
Scheme 36 Hydroxylation of 1-chloro-2,4-dinitrobenzene

Hydroxylation of m-Nitroaniline

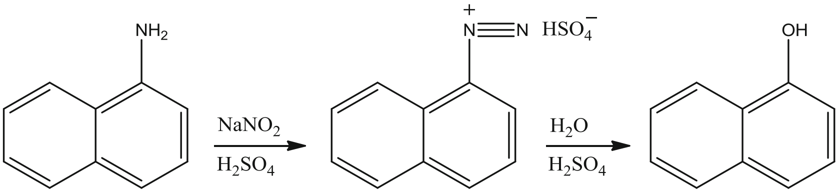
Diazonium salts undergo a large number of reactions in which the diazo group is lost as molecular nitrogen and is replaced by a variety of other groups, such as OH, I, Br, Cl, F, CN, NO_2, SO_3H, H, and Ar, which becomes attached to the aromatic ring. When a solution of diazonium salt is heated, nitrogen is evolved as gas and the diazo group is replaced by a hydroxyl group. For example, m-nitroaniline is converted to m-nitrophenol as shown in Scheme 37. The diazonium sulfate is preferred over the diazonium chloride as the presence of chloride ions gives rise to small quantities of aryl chloride as by-product. The solution must be acidic in order to avoid the coupling reaction between the unreacted diazonium salt and the phenol.

Hydroxylation of 1-Naphthylamine and 2-Naphthylamine

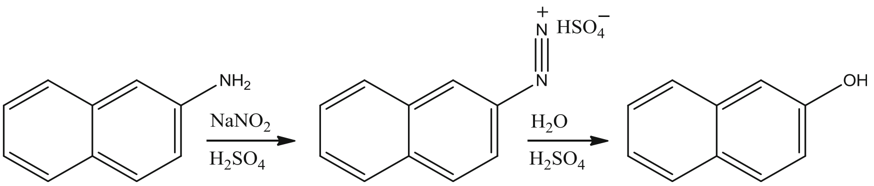
1-Naphthylamine that is diazotized with sodium nitrite and sulfuric acid followed by reaction with aqueous sulfuric acid gave 1-naphthol as shown in Scheme 38. Similarly, 2-naphthol is obtained from 2-naphthylamine as shown in Scheme 39.



Scheme 37 Hydroxylation of m-nitroaniline



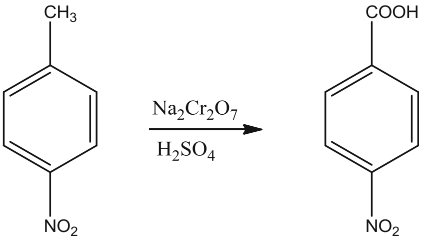
Scheme 38 Hydroxylation of 1-naphthylamine



Scheme 39 Hydroxylation of 2-naphthylamine

Oxidation

Most frequently encountered oxidation by the dye chemist is the transformation of a methyl group to carboxylic acid group (introduction of carboxylic acid group into aromatic system is called **carboxylation**) or conversion of –CH= group into keto (=C=O) group. Some of the oxidizing agents employed are summarized below: (1) air oxidation often in the presence of a catalyst; (2) chromic acid; (3) manganese dioxide (MnO_2); (4) ferric chloride ($FeCl_3$); (5) nitrosylsulfuric acid; (6) nitric acid; (7) lead peroxide; and (8) sodium hypochlorite. An alkyl group attached to the aromatic ring is oxidized to a carboxylic acid group via oxidation reaction [3–5].



Scheme 40 Oxidation of 4-nitrotoluene

Oxidation of 4-Nitrotoluene and 2-Chlorotoluene

For example, 4-nitrotoluene is oxidized with sodium dichromate in concentrated sulfuric acid to 4-nitrobenzoic acid as shown in Scheme 40.

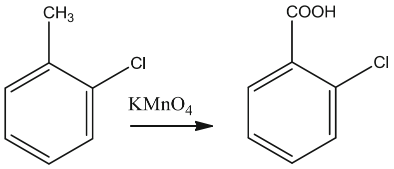
Another example of oxidation includes reaction of 2-chlorotoluene with aqueous potassium permanganate that yielded 2-chlorobenzoic acid as given in Scheme 41.

Oxidation of 2-Methylnaphthalene

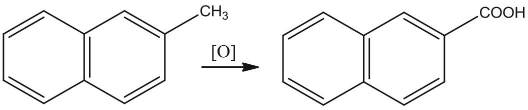
2-Methylnaphthalene is oxidized by prolonged boiling with concentrated nitric acid (HNO_3) to 2-naphthoic acid as shown in Scheme 42.

Oxidation of Naphthalene and Anthracene

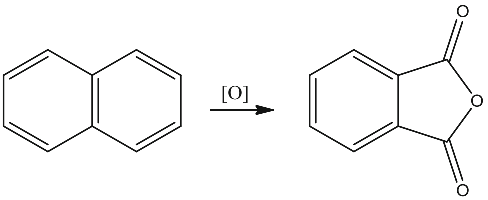
Naphthalene that is oxidized by air in the presence of a catalyst, vanadium oxide, gave phthalic anhydride as shown in Scheme 43. In a similar fashion, anthracene that is oxidized by air in the presence of catalysts, sulfuric acid and chromic acid, yielded anthraquinone as given in Scheme 44.



Scheme 41 Oxidation of 2-chlorotoluene



Scheme 42 Oxidation of 2-methylnaphthalene



Scheme 43 Oxidation of naphthalene

Halogenation

Halogen atoms, usually chlorine or bromine (rarely fluorine or iodine), are generally introduced into the aromatic systems. It is often necessary to use a catalyst. The catalyst most commonly employed is iron or ferric chloride, sometimes iron with a trace of iodine and less frequently antimony, sulfur, or phosphorus compounds [3–5]. The chloro derivatives constitute the most important class of halogen-substituted intermediates of the benzene series.

Chlorination of Toluene

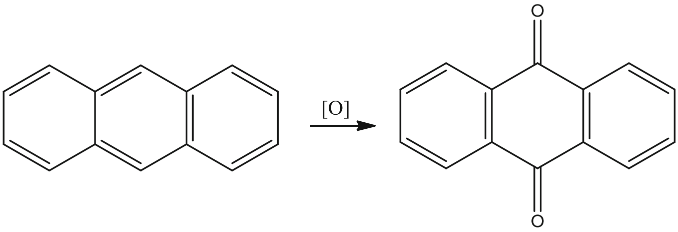
Chlorination of toluene with chlorine and ferric chloride as a catalyst resulted in approximately an equimolar mixture of o-chlorotoluene and p-chlorotoluene as given in Scheme 45.

Bromination of Benzene

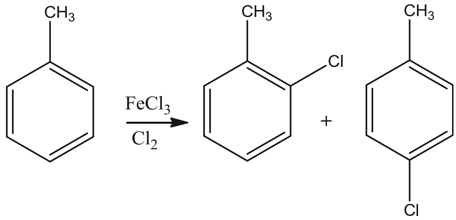
Benzene does not react appreciably with chlorine or bromine in the cold, but in the presence of catalysts such as pyridine or iron reaction takes place readily, affording mono-halogenated product. Thus, benzene reacts with bromine in the presence of pyridine as the catalyst yielded bromobenzene as shown in Scheme 46. The function of the catalyst is to increase the electrophilic activity of the halogen.

Chlorination of Naphthalene

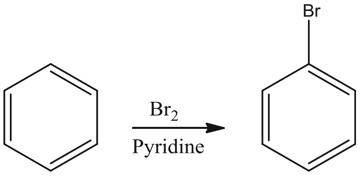
Naphthalene that is more readily chlorinated than benzene, in the presence of ferric chloride as a catalyst at 110–120 °C, gave



Scheme 44 Oxidation of anthracene



Scheme 45 Chlorination of toluene



Scheme 46 Bromination of benzene

1-chloronaphthalene as the main product along with little of 2-chloronaphthalene as side product as given in Scheme 47.

Bromination of Naphthalene

Condensed aromatic hydrocarbons are more reactive towards electrophilic reagents. For example, naphthalene can be brominated readily with bromine in carbon tetrachloride solution, and without the need of a catalyst yielded 1-bromonaphthalene as illustrated in Scheme 48.

Chlorination of Anthraquinone, 2-Methylanthraquinone, and Bromination of 1-Aminoanthraquinone

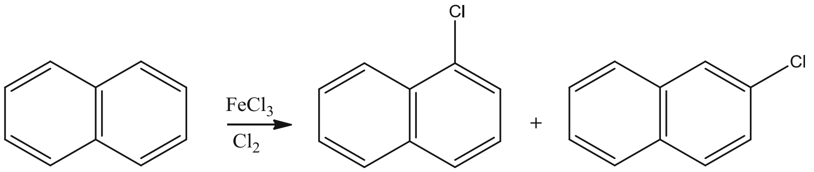
The direct chlorination of anthraquinone in oleum cannot be controlled to yield a monochloro product but instead gave 1,4,5,8-tetrachloroanthraquinone as shown in Scheme 49. Careful chlorination of 2-methylanthraquinone with chlorine and sulfuric acid yielded 1-chloro-2-methylanthraquinone as given in Scheme 50. Further, 1-aminoanthraquinone that can be readily brominated with bromine in nitrobenzene yielded 1-amino-2,4-dibromoanthraquinone as shown in Scheme 51.

Diazotization and Coupling

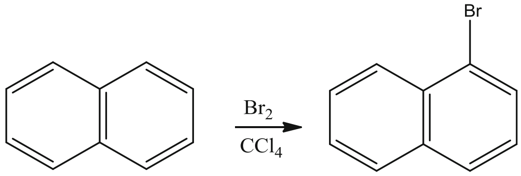
Azo dyes represent the greatest production volume of dyestuff chemistry today and their relative importance may even be growing in the future. The great success of azo dyes is due to several factors such as the simplicity of the coupling reaction, immense possibilities for structural variations and adaptation to the needs of the most diverse applications for these dyes, and often very high molar extinction coefficients of the azo dyes. Thus, the diazotization and coupling are the most important reactions in dye chemistry [3–10].

Diazotization was discovered by Griess in 1858. It is a two-step process. The first step is the formation of a diazonium salt and the second step is the coupling reaction. The aqueous solution of primary aromatic or heteroaromatic amine is treated with mineral acid (HCl, H_2SO_4) and sodium nitrite ($NaNO_2$) under ice-cold condition (0–5 °C) which gave diazonium salt as shown in Scheme 52. The use of two equivalents of acid is essential for a smooth reaction.

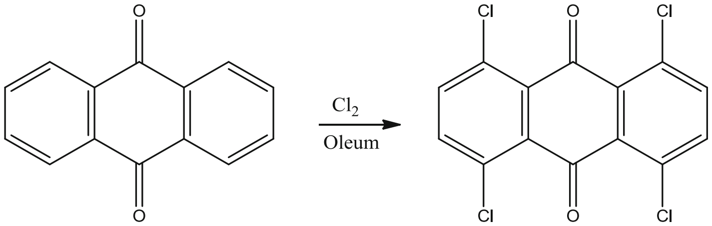
Depending on the basicity and solubility of the amine being diazotized, there are several types of diazotization as given below:



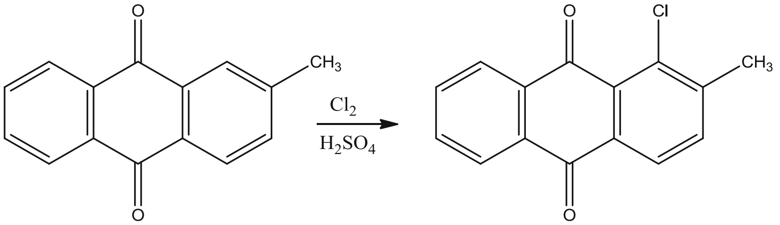
Scheme 47 Chlorination of naphthalene



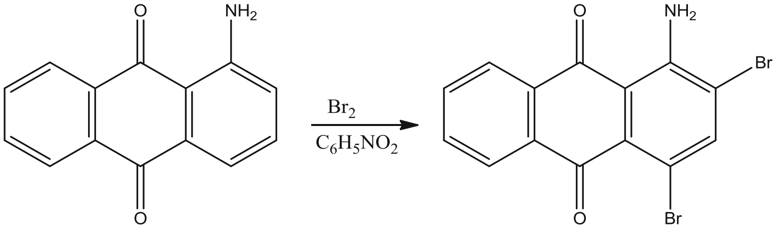
Scheme 48 Bromination of naphthalene



Scheme 49 Chlorination of anthraquinone



Scheme 50 Chlorination of 2-methylanthraquinone



Scheme 51 Bromination of 1-aminoanthraquinone

$$\mathrm{R{-}NH_2} + 2\,\mathrm{HX} + \mathrm{NaNO_2} \longrightarrow \mathrm{R{-}\overset{+}{N}{\equiv}N}\ \mathrm{X}^{-} + \mathrm{NaX} + 2\,\mathrm{H_2O}$$

R = Aryl, hetaryl; X = Cl, Br, NO_3, HSO_4

Scheme 52 Diazotization

Direct Diazotization

The name "direct" is entirely arbitrary. The primary aromatic or heteroaromatic amine is dissolved or suspended in aqueous hydrochloric or sulfuric acid and aqueous solution of sodium nitrite is added. A temperature of 0–5 °C is maintained by adding ice and salt. Simplicity, speed, and cheapness are the advantages to be gained by its use, but it is not for isolation of the diazonium compounds in the solid form.

Inverted or Indirect Diazotization

The primary aromatic or heteroaromatic amines with carboxylic acid or sulfonic acid groups are often difficult to dissolve in dilute acid. Therefore, the amine is dissolved in water or weak alkali and calculated amount of sodium nitrite solution is added to this amine solution, which is stirred at 0–5 °C adding ice and salt. Thus, the reactivity of the amine is increased by alkali; hence, the method is called "inverted" or "indirect." The acid can also be added to amine-nitrite mixture. Diazotization usually takes place instantly.

Diazotization of Weakly Basic Amines

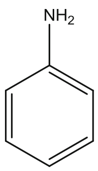
When the basicity of an amine is so much reduced that it is no longer soluble in aqueous acids because its salts suffer complete hydrolytic dissociation, the use of such media for diazotization becomes impossible. Weakly basic amines are soluble only in concentrated acids and diazotization is carried out in such solution. Concentrated sulfuric acid is the most commonly employed solvent for this purpose. Thus, nitrosylsulfuric acid is prepared from solid sodium nitrite and concentrated sulfuric acid and used for diazotization. Weakly basic amines are dissolved in concentrated sulfuric acid and diazotized with nitrosylsulfuric acid.

Diazotization in Organic Solvents

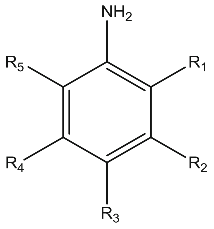
The water-insoluble or sparingly soluble amine is dissolved in organic solvents (alcohol) or glacial acetic acid and diluted with water. After the addition of acid, it is diazotized in the usual manner with sodium nitrite solution.

Aromatic Diazo Components

Anilines, substituted anilines, naphthylamines, and substituted naphthylamines are used as aromatic diazo components. The representative examples of aromatic diazo components are aniline, substituted anilines, 1-naphthylamine, substituted 1-naphthylamines, 2-naphthylamine, and substituted 2-naphthylamines as shown below.

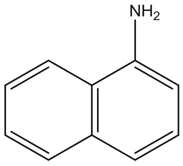


Aniline

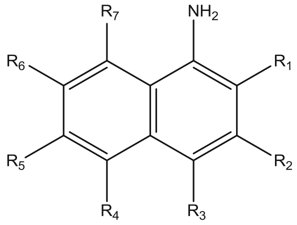


R_1, R_2, R_3, R_4, R_5 = H, halogen, alkyl, alkoxy, NO_2, SO_3H

Aniline Derivatives

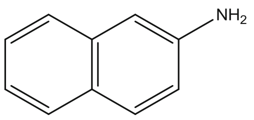


1-Naphthylamine

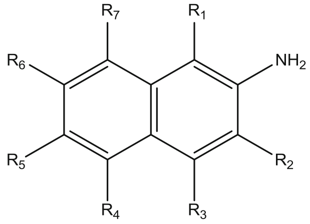


R_1, R_2, R_3, R_4, R_5, R_6, R_7 = H, halogen, alkyl, alkoxy, $NHCOCH_3$, NO_2, SO_3H

1-Naphthylamine Derivatives



2-Naphthylamine

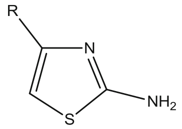


R_1, R_2, R_3, R_4, R_5, R_6, R_7 = H, halogen, alkyl, alkoxy, $NHCOCH_3$, NO_2, SO_3H

2-Naphthylamine Derivatives

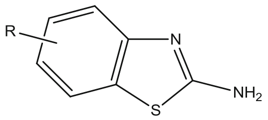
Heterocyclic Diazo Components

Dyes with heterocyclic diazo components have received much attention because of their high tinctorial power and excellent brightness. Heterocyclic diazo components are used in the preparation of acid dyes for polyamide carpet fibers, which demonstrated excellent leveling properties. Heterocyclic diazo components are also extensively used in the preparation of disperse dyes with outstanding dischargeability on cellulose acetate fibers. The success of new diazo components has been especially remarkable with disperse dyes as it has become possible to cover the whole shade range with monoazo dyes. These new monoazo blue dyes can now replace anthraquinones. The representative examples of heterocyclic diazo components are 2-aminothiazoles, 2-aminobenzothiazoles, 5-aminoisothiazoles, 3-amino-2,1-benzoisothiazoles, 2-amino-1,3,4-thiadiazoles, 5-amino-1,2,4-thiadiazoles, 2-aminoimidazoles, 5-aminopyrazoles, 2-aminothiophenes, 3-aminothiophenes, 2-aminothiazoles, and 2-aminobenzothiazoles [11] as shown below.



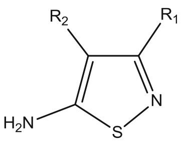
R = H, alkyl, aryl

2-Aminothiazoles



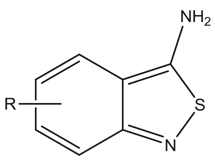
R = H, halogen, alkyl, alkoxy, aryl, NO_2, NH_2, $NHCOCH_3$, SO_3H

2-Aminobenzothiazoles



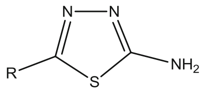
$R_1 = CH_3$; $R_2 = CN$

5-Aminoisothiazoles



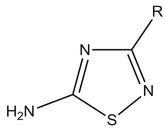
R = H, alkyl

3-Amino-2,1-benzoisothiazoles



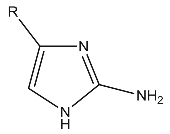
R = H, alkyl, aryl

2-Amino-1,3,4-thiadiazoles



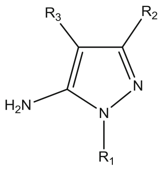
R = H, alkyl, S-alkyl, aryl

5-Amino-1,2,4-thiadiazoles



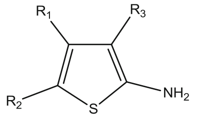
R = H, alkyl, aryl

2-Aminoimidazoles



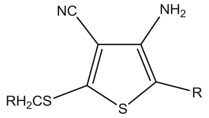
R_1, R_3 = H, alkyl, aryl; R_2 = CN, COOalkyl

5-Aminopyrazoles



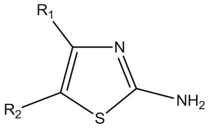
R_1, R_2 = H, alkyl, aryl, cycloalkyl, hetaryl;
R_3 = CN, COOH, COOalkyl, COOaryl, $CONH_2$

2-Aminothiophenes



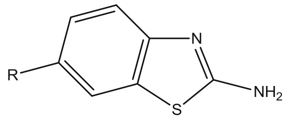
R = CN, NO_2

3-Aminothiophenes



R_1, R_2 = H, alkyl, aryl, CN, NO_2, CHO

2-Aminothiazoles



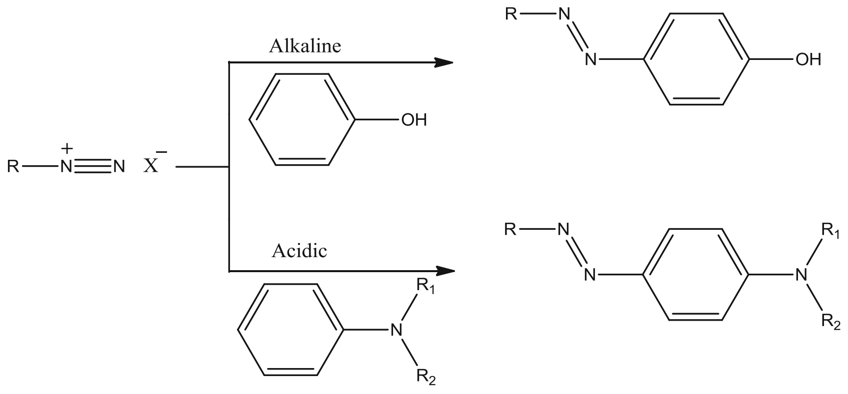
R = H, alkyl, aryl, NO2, CN,
$SO_2CH_2CH_2OH$, $SO_2CH_2CH_2CN$

2-Aminobenzothiazoles

Coupling

Coupling was discovered by Kekule and Hidegh in 1870. The optimum coupling conditions depend on the nature of the diazo and coupling components used. The acidic diazonium salt solution is very slowly added (dropwise) to a solution of coupling component, either in acid or in alkali depending on the type of coupling component desired. The coupling reaction may be completed immediately after the components are mixed or after several hours. The monitoring and control of pH are extremely essential for coupling reaction. It is critical to maintain temperature at 0–5 °C by adding ice-salt mixture. The control of reaction temperature and pH is extremely necessary for the smooth coupling reaction. Coupling takes place in two ways, alkaline coupling and acidic coupling. In alkaline coupling, the diazonium salts couple to p-position of the hydroxyl group (or if p-position is occupied then it couples to o-position). In acidic coupling, the diazonium salts couple to p-position of the N,N-dialkyl-substituted aryl amines as shown in Scheme 53.

The coupling components include aromatic hydroxy compounds such as phenols, naphthols, naphtholsulfonic acids, aromatic amines such as anilines, diaminobenzenes, naphthylamines, naphthylaminesulfonic acids, aromatic aminophenols, aminophenolsulfonic acids, aminonaphtholsulfonic acids, aromatic N, N-dialkylsubstituted aryl amines, compounds with reactive methylene group (acetoacetarylides), and heterocyclic coupling components such as 5-hydroxypyrazoles, 5-aminopyrazoles, 6-hydroxypyridines, 6-aminopyridines, hydroxypyrido[1,2-a]benzimidazoles, aminopyrido



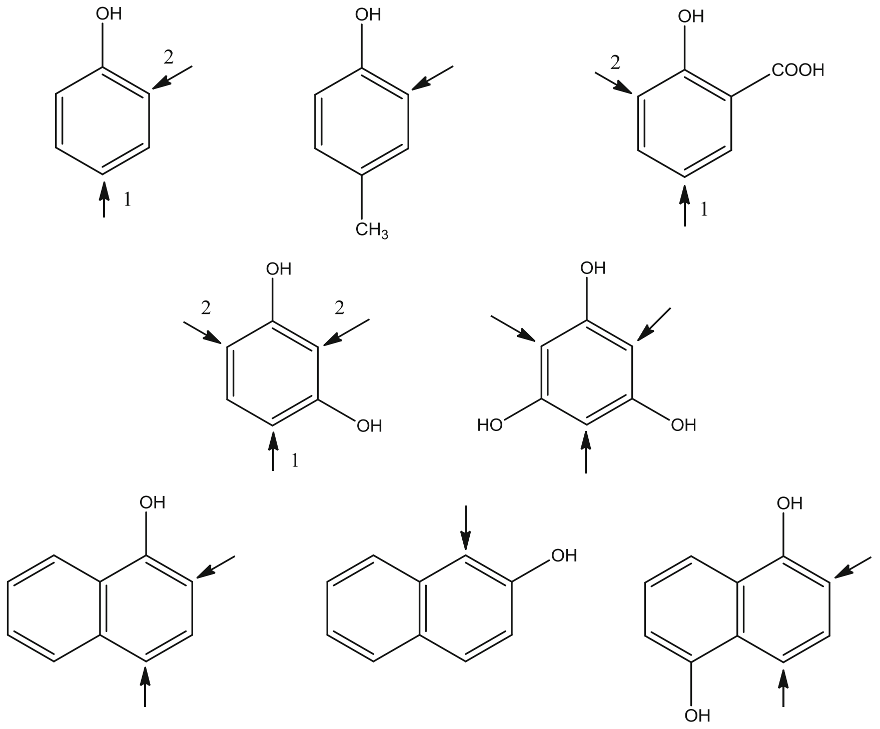
R = Aryl, hetaryl; X = Cl, Br, NO_3, HSO_4; R_1, R_2 = alkyl, CH_2CH_2OH, CH_2CH_2CN

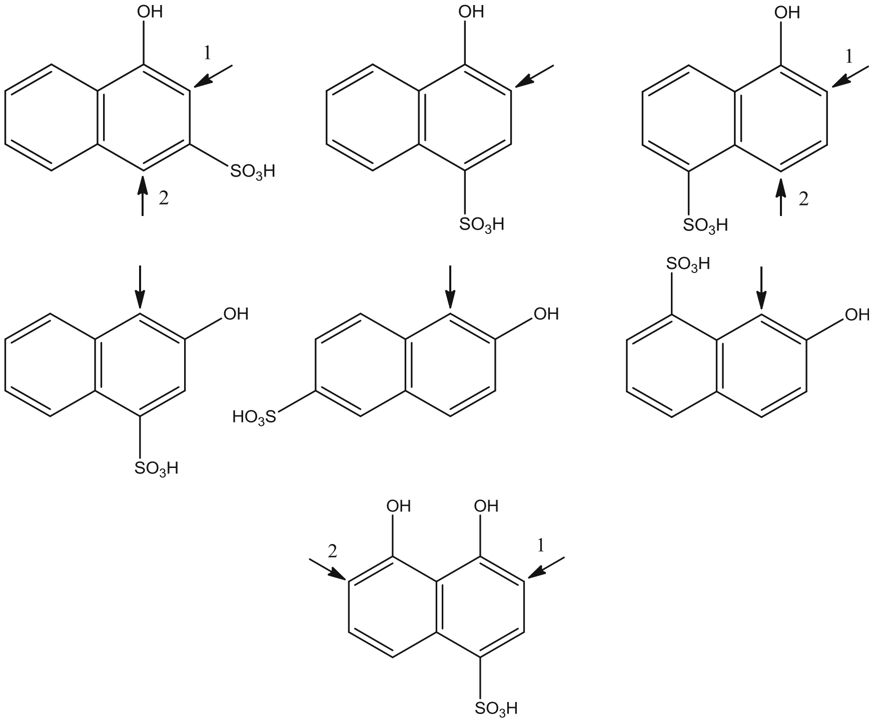
Scheme 53 Coupling at alkaline and acidic pH

[1,2-a]benzimidazoles, hydroxypyrimidines (barbituric acid), and hydroxyquinolines/ hydroxyquinolones that are discussed below.

Aromatic Hydroxy Compounds

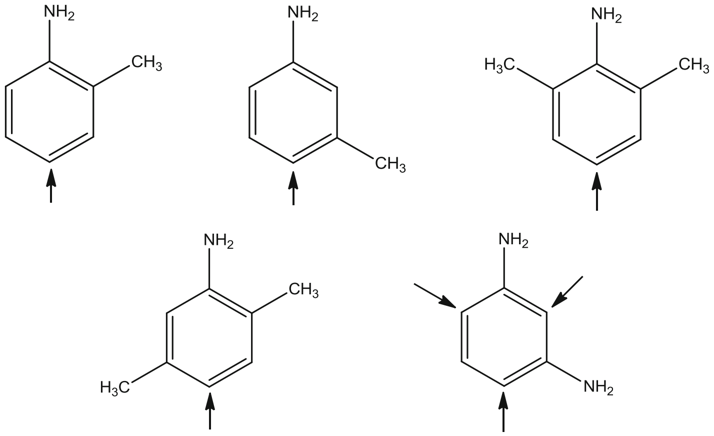
This group includes aromatic hydroxy compounds such as phenols, naphthols, and naphtholsulfonic acids, in which the coupling is carried out at the alkaline pH. Phenols mainly couple at the 4-position or at the 2-position if the 4-position is occupied. 1-Naphthols mainly couple at 4-position but 2- and 2,4-coupling products are also obtained, depending on the diazo component. 2-Naphthol couples at the 1-position. Similarly, the coupling of naphtholsulfonic acids is as shown below.

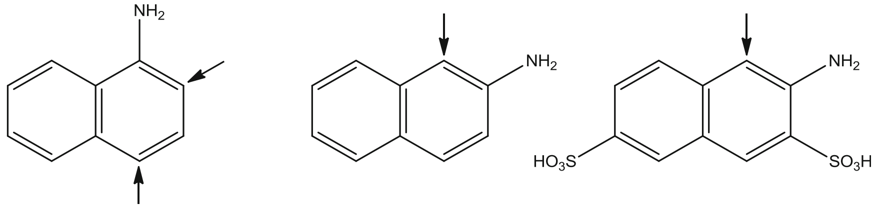




Aromatic Amines

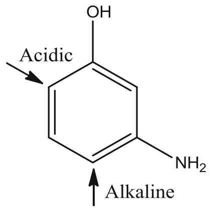
This group includes aromatic amines such as anilines, diaminobenzenes, naphthylamines, and naphthylaminesulfonic acids, in which the coupling is carried out at the acidic pH. Anilines mainly couple at the 4-position or at the 2-position if the 4-position is occupied. 1-Naphthylamines mainly couple at 4-position but 2- and 2,4-coupling products are also obtained, depending on the diazo component. 2-Naphthylamine couples at the 1-position



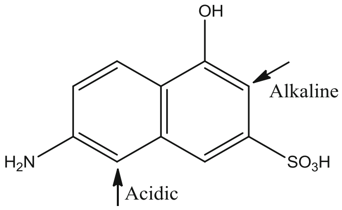


Aromatic Aminophenols, Aminophenolsulfonic Acids, Aminonaphtholsulfonic Acids

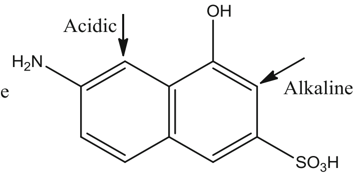
In acidic medium, the coupling occurs at ortho or para position to amino group while the coupling occurs at ortho or para position to hydroxy group in alkaline medium. The preference of whether acidic or alkaline coupling occurs first depends on the other substituents on the aromatic nucleus as shown below. The representative examples of aromatic aminophenols, aminophenolsulfonic acids, and aminonaphtholsulfonic acids are *m*-aminophenol, I acid, γ acid, H acid, and K acid as shown below.



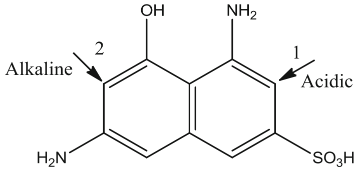
m-Aminophenol



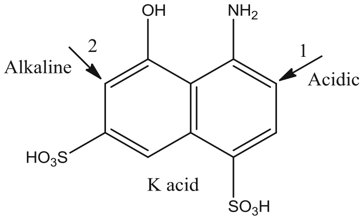
I acid



γ acid



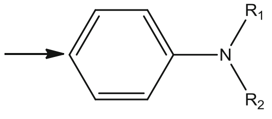
H acid



K acid

Aromatic N,N-Dialkylsubstituted Aryl Amines

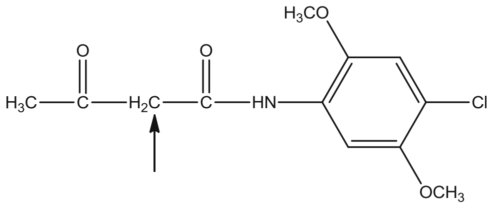
The coupling occurs at p-position of N, N-dialkylsubstituted aryl amines under acidic conditions. The representative examples of aromatic N,N-dialkylsubstituted aryl amines are as shown below.



R_1, R_2 = alkyl, CH_2CH_2OH, CH_2CH_2CN

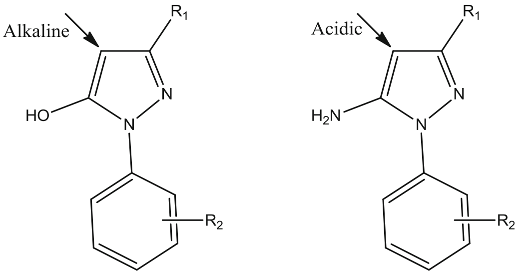
Compounds with Reactive Methylene Group

The coupling occurs at the reactive methylene group (>CH_2). N-acetoacetyl derivatives of aromatic amine (acetoacetarylides) have the greatest industrial importance. Anilines substituted with halogen, alkyl, alkoxy, nitro, and acylamino groups are most commonly used as shown below.

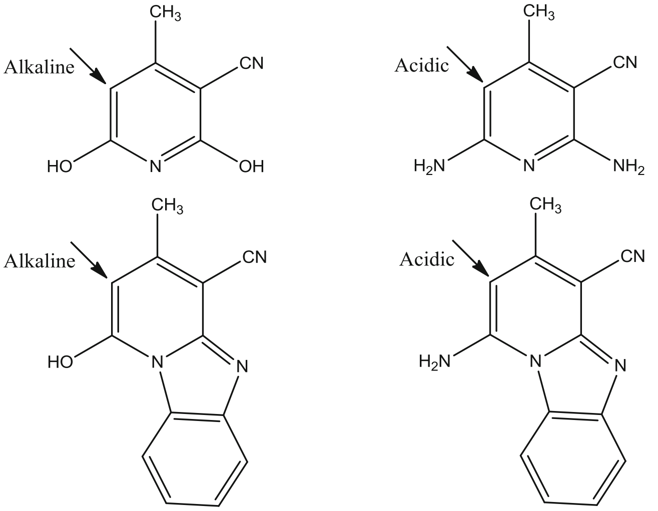


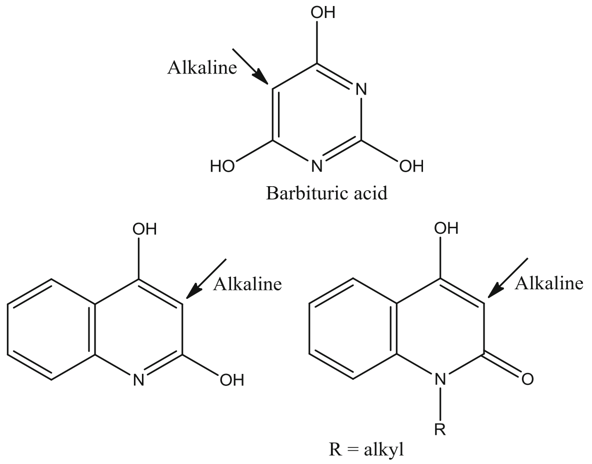
Heterocyclic Coupling Components

As the great majority of the azo dyes are synthesized by the coupling reaction, the progress in azo dye chemistry has been largely determined by the technological progress in coupling. New azo coupling components and in particular new heterocyclic coupling components are of tremendous importance. The most commonly used heterocyclic coupling components with highest technical importance and for generating brightest dyes are discussed below. The representative examples of heterocyclic coupling components are 5-hydroxypyrazoles, 5-aminopyrazoles, 6-hydroxypyridines, 6-aminopyridines, hydroxypyrido[1,2-a]benzimidazoles, aminopyrido[1, 2-a]benzimidazoles, hydroxypyrimidines (barbituric acid), and hydroxyquinolines/ hydroxyquinolones [12] as shown below.



R_1 = alkyl; R_2 = H, Cl, alkyl, SO_3H





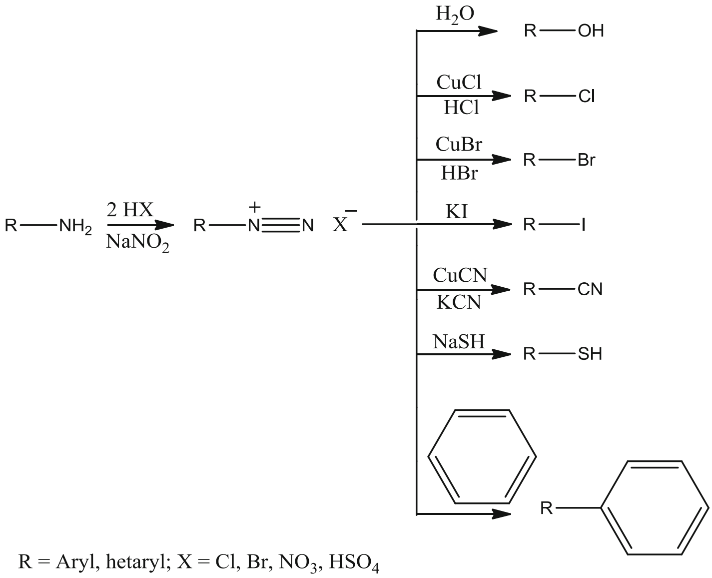
Replacement of Diazo Group by Other Groups

Diazonium salts undergo a large number of reactions in which the diazo group is lost as molecular nitrogen and is replaced by a variety of other groups, e.g., OH, Cl, Br, I, CN, SH, and C_6H_5, which becomes attached to the aromatic ring as shown in Scheme 54.

Dyeing

It is difficult if not impossible to determine when mankind first systematically applied color to a textile substrate. The first colored fabrics were probably nonwoven felts painted in imitation of animal skins. The first dyeings were probably actually little more than stains from the juice of berries. Ancient Greek writers described painted

Scheme 54 Replacement of diazo group by other groups



R = Aryl, hetaryl; X = Cl, Br, NO_3, HSO_4

fabrics worn by the tribes of Asia Minor. But just where did the ancient craft have its origins? Was there one original birthplace or were there a number of simultaneous beginnings around the world?

Although it is difficult to determine just when each respective civilization began to use dyes, it is possible to date textile fragments and temple paintings, which have survived the ensuing centuries. The ancient Egyptians wove linen as early as 5000 BC, and paintings on tomb walls infer that colored wall hangings were in use by 3000 BC. By 2500 BC, dyer's thistle and safflower were used to produce red and yellow shades. Egyptian dyers developed a full range of colors by 1450 BC.

Another cradle of civilization was the Indian subcontinent where religious and social records dating to 2500 BC refer to dyed silk and woven brocades of dyed yarn. Cotton, first cultivated in the Indus valley of Pakistan, was woven as early as 2000 BC. A book written around 300 BC included a chapter on dyes. It is believed that systematic dyeing occurred in China as early as 3000 BC near the city of Xian in the Hoang (Yellow) River Valley, although there is no conclusive proof. Empress Si-Ling-Chi is credited with the discovery of silk about 2640 BC. Kermes and indigo were used as dyes as early as 2000 BC. Fragments of silk have been found in the corrosive patina of bronze swords of the Shang dynasty (1523–1027 BC), but most assuredly these samples are not the oldest [13].

The New World was similarly active in developing the textile art. With help from the desert climate in the high Andes of Peru, dyed samples of wool have been preserved and recovered from burial sites. These fragments have been dated to the millennium before the Christian era. The western and southwestern regions of the United States provided homes for the Anasazi, or ancient ones, who dwelt in the region of Mesa Verde National Park in southwestern Colorado, northern Arizona, New Mexico, and eastern Utah. Again the dry climate has helped to preserve samples from these early civilizations.

Very little in the nature of large, intact textile samples has survived in Europe. Remains of a large woolen robe, the Thorsberg Robe, found in northern Germany and dated prior to 750 BC, indicate a highly developed dyeing and weaving technology [14]. Indirect evidence is more plentiful: for example, a tombstone of a purpurarius, a Roman purple dyer, was found near Parma, northern Italy, and a dyer's workshop excavated in Pompeii. This great center of the Roman Empire was destroyed by the eruption of Mount Vesuvius in 79 AD. Similar stone vats for dyeing have been excavated in the tells of Israel and in present-day Turkey.

The Dark Ages following the fall of the Roman Empire were dark indeed, with little development of the dyer's art. The robes of a number of the monastic orders were brown and black, surely a dark age. By the end of the 1300s, however, civilization began making the swift and certain strides that have led to our present level of development. In 1371, the dyers of Florence, a city famous for its Renaissance art, formed a guild, or association of like merchants and craftsmen, which lasted for 11 years. Other guilds were being formed in other centers across Europe. Some of these guilds exist to this day. The Worshipful Company of Dyers was formed in 1471 in London. One of the legacies of this guild is a Publications Trust, which has underwritten the publication of a number of books on dyeing in cooperation with The Society of Dyers and Colourists.

The art and craft of dyeing were largely passed down from father to son or from craftsman to apprentice by word of mouth and example until the early 1500s. The *Plictho* of Gioanventura Rosetti, a Venetian armory superintendent, is believed to be the first published book on dyeing. It certainly is the oldest surviving European text to have come down to us in the twenty-first century. Five known Italian editions were published between 1548 and 1672. A French edition appeared in 1716. It is interesting that no known English translation was made until 1968 [15] when Sidney Edelstein of the Dexter Chemical Company and Hector Borghetty collaborated to reproduce a facsimile of the original 1548 edition along with a complete translation into English. During his extensive travels, Rosetti collected dyeing recipes and processes used in the flourishing city states of Venice, Genoa, and Florence. He published: *Plictho de L'arte de Tentori che insegna tenger pani telle banbasi et sede si per larthe magiore come per la comune* or *Instructions in the Art of the Dyers, Which Teaches the Dyeing of Woolen Cloths, Linens, Cottons, and Silk by the Great Art as Well as by the Common* or simply *Instruction in the Art of Dyeing*. The book was divided into four sections: the first and second sections were devoted to the dyeing of wool, cotton, and linen; the third to the dyeing of silk and the use of fugitive colors; and the fourth to the dyeing of leather and skins. Approximately 160 complete recipes were preserved in the first three sections. Edelstein and Borghetty labored diligently in determining the meanings of terms in recipes written in the dialect of sixteenth-century Italy.

Synthetic Dyes

The father of modern synthetic dyes was William Henry Perkin (1838–1907), who synthesized mauve, or aniline purple, in 1856. The story behind this great story bears telling. William's father was a builder who wanted him to become an architect, but like many others, Perkin did not follow his father's chosen profession. Perkin studied at the City of London School where he became interested in chemistry at the age of 12. A teacher, Mr. Hall, gave him work in the laboratory, which in turn inspired Perkin to follow his natural curiosity. At age 15, Perkin entered the Royal College of Science and listened to the lectures of the great German chemist, August Wilhelm von Hofmann (1818–1892). He was granted an assistantship under von Hofmann at age 17. Because his work did not allow time for his own research, he set up a separate laboratory at home and it was there that he discovered aniline purple, the first dyestuff to be commercially produced. Another dye, based on naphthalene, and prepared in collaboration with Arthur H. Church, actually preceded aniline purple, but was not commercially produced before aniline purple. Aniline purple was discovered at this home during Easter vacation while looking for quinine, an antimalarial drug. After oxidizing aniline with potassium dichromate and getting a black precipitate, extraction with ethanol gave a brilliant purple solution. Almost immediately, he sent a sample of this dye to a dyer in Perth with a request to dye silk fabric. The dyer's report read: “If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a long time.” Trials on cotton were not as successful because the need for a mordant was not realized. Perkin later reported, “The value of mauve was first realized in France, in 1859. English and Scotch calico printers did not show any interest in it until it appeared on French patterns, although some of them had printed cloth for me with that colour [16].”

Since that beginning, thousands of dyes have been synthesized; some 1500–2000 are commercially successful today. Until 1884, however, all synthetic dyes required a mordant to give acceptable wash-fastness on the textile substrate. In 1884, Böttiger produced Congo red, which could dye cotton directly without a mordant. These dyes were commonly called direct dyes. In order to improve wash-fastness, the path taken in some synthetic dye chemistry was to build the dye from two or more components, directly in the fiber, or in situ. By building a large molecule without solubilizing groups within the fiber, wash-fastness was markedly improved. The first practical development along these lines was by A. G. Green who synthesized primuline, a dye that because of poor light-fastness was not commercially important but later led the way to many important commercial dyes. Table 2 lists a number of classes of dyes along with the date of discovery. Worldwide, 80% of all dyes go into textiles and 20% into paper, leather, food, and the like.

Development of US Dyestuff Industry

The natural dye industry was more than just a cottage industry in Colonial America. Indigo was

Table 2 Dyes in order of discovery

Basic: Mauve or aniline purple, Perkin, 1856; Fuchsin, Verguin, 1859
Acid: Alkali blue, Nicholson, 1862
Vat: Alizarin, Gräbe & Liebermann, 1868
Indigo, von Bayer, 1880, discovered structure and synthesized indigo
Indanthrene, Böhn, 1901
Direct: Congo red, Böttiger, 1884
Direct developed: Primuline coupled with beta-naphthol, Green, 1887
Sulfur: Vidal, 1893
Azoics: Zitscher & Laske, 1911
Disperse: A simple azo dye, 1920s
Phthalocyanine: Linstead & Diesbach, 1928–1929
Reactive: Commercialized, I.C.I., Rattee and Stevens, 1956

a very important cash crop in South Carolina among the coastal islands and for some distance inland. Plantations existed well into the early 1900s despite the growth of the synthetic dyestuff industry.

The modern synthetic dye industry in the United States dates from World War I. However, in 1864, Thomas Holliday of Great Britain, and in 1868, the Albany (NY) Aniline Company with participation of Bayer of Germany began coal-tar dye manufacture. In the early 1900s, most synthetic dyes used in the United States were imported from Germany and Switzerland. With the outbreak of World War I, the British naval blockade of Germany prevented export of dyes from Europe. In spite of the blockade, the German submarine, *Deutschland*, ran the British blockade and sailed into American ports twice with dyestuffs and drugs. The Germans needed critical war material and export moneys; the United States and others needed dyes. Ironically, in 1914, German dyes were used by French dyers to dye the official French Army uniforms. The outbreak of war and ensuing blockade showed the United States how important dyes were to the American economy. Several companies began investigative work that would lead to dye synthesis; they found that dyestuffs were very difficult to make; the chemistry was much more complex than imagined. A real boost to the US industry came after World War I, when the German patents were given over to the Allies via the Alien Property Custodian. According to Lehner, DuPont reportedly spent $43 million, a tremendous sum of money in the early twentieth century, before ever showing a profit [17]. Obviously, only financially strong companies could afford to enter the business. The early pioneers included Allied (formed by merging five companies), American Cyanamid, and DuPont, to name only a few who survived to become major factors later in the twentieth century. In 1938, others included Dow, German-owned General Aniline and Film (GAF), and Swiss-owned Cincinnati Chemical Company (Ciba, Geigy, and Sandoz). In the 1960s, 50–60% of all US manufacturing was in the hands of four principal US companies:

- Allied Chemical (later sold to Bayer of Germany and to independent investors as Buffalo Color, 1977)
- American Cyanamid
- GAF, the result of the break-up of the German cartel, I. G. Farben, which was nationalized during World War II and sold to BASF in 1978
- DuPont (sold in 1980–1981 with various lines going to Crompton & Knowles, Ciba, and Blackman-Uhler)

Today, there are at least 42 dyestuff manufacturers, distributors, and repackaging agents in the United States [18]. Of the major companies, Swiss and German-based companies tend to dominate the US market. Those companies include:

- Ciba, formerly Ciba-Geigy, Switzerland
- Clariant (split off from Sandoz in 1995), Switzerland
- DyStar, formed by the merger of Hoechst and Bayer (1995), acquisition of BASF textile colors which include the former Zeneca, and Mitsubishi of Japan
- Crompton & Knowles sold to Yorkshire Group Plc and is now Yorkshire Americas

There is no major surviving US-based company. Raghavan [19] and Mock [20] give an interesting description of these mergers and the reasons behind them.

Most of the international companies have limited manufacturing facilities in the United States and major facilities in other countries where environmental laws are not as stringent or where the parent companies have a modern integrated low-pollution facility. These facilities in the United States minimize the tariffs paid and also allow quicker response to the marketplace. Ciba has a manufacturing facility in St. Gabriel, LA; Clariant in Martin, SC; DyStar near Charleston, SC; and Yorkshire Americas at Lowell, NC.

Today well over 1500 dyes are produced in commercial quantities, although only a select handful in each class are the true "workhorse" colors found in virtually every dyehouse dyeing a particular substrate for a particular end use. Approximately two-thirds of the dyes and pigments consumed in the United States are used by the textile industry. One-sixth of the dyes and pigments are used for coloring paper, and the rest are used chiefly in the production of organic pigments and in the dyeing of leather and plastics.

Dyes are catalogued and grouped under a set of rules established by the Colour Index committee, consisting of representatives from the Society of Dyers and Colourists (SDC), Bradford, England, and the American Association of Textile Chemists and Colorists (AATCC), Research Triangle Park, NC. Table 3 shows how over 9000 dyes are enumerated in the Colour Index. The Colour Index, now in its fourth edition, is updated periodically with newly released information and is available in book form and on CD-ROM. Volumes 1–3, published in 1971, contain the C.I. name and number, chemical class, fastness properties, hue indication, application, and usage. Volume 4, also published in 1971, contains the structures of all disclosed structures. Volume 5, last published as part of Volume 9 in 1993, contains the commercial names of all known dyes and pigments. Volumes 6–8 are supplements with updates to information in Volumes 1–4 up to 1976, 1981, and 1987, respectively. An online version of the Colour Index containing a significant number of new entries was made available in 2002.

In addition to the Colour Index, AATCC publishes a *Buyer's Guide* annually in July [18]. Part A lists dyes, pigments, and resin-bonded pigment colors available from companies who choose to list this information.

The textile industry uses a large number of dyestuffs from each of the dye categories, the choice depending on the shade, fiber, and dyeing process; end use of the textile product; requirements for fastness; and economic considerations. To provide an understanding of the interrelationships that exist among the various dye classes and fiber types, a brief survey of the major fibers follows.

A review describes the textile dye industry in the United States. [21]. The market for dyes continued to shrink in the United States during the late 1990s. It seems clear that apparel production has essentially left the United States for the

Table 3 Dyes listed in the Colour Index

Shade	Yellow	Orange	Red	Violet	Blue	Green	Brown	Black	Sum
Acid	255	178	439	131	356	121	453	236	2169
Direct	171	121	263	104	303	100	242	189	1493
Disperse	243	155	371	102	371	9	27	31	1309
Reactive	188	123	252	44	250	27	48	46	978
Pigment	194	69	262	50	74	52	42	32	775
Basic	108	68	115	50	164	6	23	11	545
Vat	48	29	61	17	74	44	84	65	405
Sulfur	23	5	14	–	20	37	96	18	213
Mordant	65	47	95	60	82	36	92	96	573
Natural	26	4	34	–	–	5	13	–	82
Solvent	174	105	232	49	134	33	58	52	837
Food	15	8	17	–	5	4	3	3	55
Total									9475

foreseeable future; over 80% are currently of foreign origin. Dyes will continue to be used in the United States in carpet, upholstery, bed linens, and home furnishings; however the non-textile uses of dyes continue to increase in the United States.

Textile Fibers

In this survey, commercially important textile fibers are grouped by their origin. First there are the natural fibers from plant sources, cotton and flax, and those from animal sources, wool and silk. A second group consists of those fibers that are regenerated or chemically modified natural materials, the rayon and acetate fibers. The final group consists of synthetic fibers, which include polyester, nylon, acrylics, polyolefins, and elastane.

Natural Fibers

Cotton. Cotton fibers are comprised mainly of cellulose, a long-chain polymer of anhydroglucose units connected by ether linkages. The polymer has primary and secondary alcohol groups uniformly distributed throughout the length of the polymer chain. These hydroxyl groups impart high water absorption characteristics to the fiber and can act as reactive sites. The morphology of the cotton fiber is a complex series of reversing spiral fibrils. The fiber in total is a convoluted collapsed tube with a high degree of twist occurring along the length of the fiber. This staple fiber occurs in nature in lengths of ½–2 in., depending on the variety and growing conditions. The diameter ranges from 16 to 21 μm (1 μm is 1×10^{-6} m).

Flax. Flax is also a cellulosic fiber but has a greater degree of crystallinity than cotton. The morphology of flax is quite different from that of cotton. Flax fibers have a long cylindrical shape with a hollow core. The fibers range in length from ½ to 2½ in., with a diameter of 12–16 μm. Flax staple is comprised of bundles of individual fibers. Historians believe that flax was among the first fibers to be used as a textile fiber. In recent years, its commercial importance as a textile fiber has decreased significantly.

Wool. Wool fibers are comprised mainly of proteins: the polypeptide polymers in wool are produced from some 20 alpha-amino acids. The major chemical features of the polypeptide polymer are the amide links, which occur between the amino acids along the polymer chain, and the cystine (sulfur to sulfur) cross-links, which occur in a random spacing between the polymer chains. The polymer contains many amine, carboxylic acid, and amide groups, which contribute in part to the water-absorbent nature of the fiber.

The morphology of wool is complex. There is an outer covering over the fiber, the cortical. There are also overlapping scales having a ratchet configuration that causes shrinkage and felting. The coefficient of friction in wool fibers is vastly different between the tip and the root, depending on which way the scales point. Wool can be made washable by chemically abrading the scales or coating the fibers with another polymer.

Wool fibers are not round but are oval in cross section. The cortical cells constitute the major component of the fiber, and are aligned along the axis of the fiber. There is a medulla section at the center region of the fiber. Each fiber has a bicomponent longitudinal crystalline arrangement. One side of the fiber contains alpha-keratin crystalline regions, and the other contains beta-keratin crystalline regions. Alpha-keratin and beta-keratin have different moisture absorption characteristics, and this difference is what gives wool fibers crimp and springiness. It is also the reason why wool fibers kink in conditions of high humidity.

Wool fibers are sheared from about 30 major sheep breeds. The length of the wool fibers varies from 1 to 14 in. and depends on the breed, climate, and location on the sheep's anatomy. The fibers can be very fine to very coarse, ranging from 10 to 50 μm in diameter. The longer, coarser fibers normally are used for woolen fabrics, whereas the shorter finer ones are used for worsted fabrics.

Silk. Silk, like wool, is a protein fiber, but of much simpler chemical and morphological makeup. It is comprised of six alpha-amino acids, and is the only continuous-filament natural fiber. Historians claim that silk was discovered in China in 2640 BC. Silk fiber is spun by the silkworm as a smooth double strand, each part having a trilobal cross section. This configuration helps give silk its lustrous appearance. The fiber is unwound from the cocoon the silkworm spins as it prepares its chrysalis. The filaments are smooth and have no twists in their length, which can vary from 300 to 1800 yards. The diameter of silk is very fine, ranging from 2 to 5 μm. Because of the labor-intensiveness of sericulture and subsequent preparation of the fiber, silk remains a luxury fiber.

Regenerated Fibers

Rayon. Viscose rayon, like cotton, is comprised of cellulose. In the manufacturing process, wood pulp is treated with alkali and carbon disulfide to form cellulose xanthate. Subsequently, the reaction mass is forced through a spinneret and precipitated in an acid coagulation bath as it is formed into a continuous filament. The fiber has a round striated cross section. Rayon staple is made by "breaking" the continuous strands into staple-length fibers. Viscose rayon is conventionally produced in diameters varying from 9 to 43 μm.

Acetate. Triacetate and diacetate fibers are manufactured by the chemical treatment of cellulose obtained from refined wood pulp or purified cotton lint. Most of the hydroxyl groups are acetylated (esterified) by treating the cellulose with acetic acid. This determines the chemical configuration of triacetate. Acetate or diacetate is made by the saponification of one of the acetylated groups, thus restoring a hydroxyl to each cellulosic monomer unit. Theoretically, then, diacetate has two acetylated groups in each glycoside unit. The conversion of the hydroxyl groups causes these fibers to be hydrophobic and changes the dyeing characteristics drastically from those of the normal cellulosic fibers.

Triacetate fibers are spun by mixing the isolated reaction product (flake) with methylene chloride and alcohol. The spinning solution (dope) is forced through a spinneret and dry-spun into continuous filaments.

An alternate way of wet spinning is also possible. Acetate fibers are spun by mixing the isolated reaction product with acetone and water. The spinning solution is formed into filaments by evaporating the solvent and coagulating the acetate in a manner similar to that for triacetate (i.e., by the dry-spinning method).

Synthetic Fibers

Nylon. In 1939 the DuPont Company introduced the first truly synthetic textile fiber. Dr. Wallace Carothers invented nylon as a result of his basic research into polymer science. Chemically, nylon is a polyamide fiber. The two major types of nylon polymer are used in textiles: type 6,6 which is made by using hexamethylenediamine and adipic acid, and type 6, which is made by polymerizing ε-caprolactam. Nylon fibers are made by melt-spinning the molten polymer. The result is a continuous filament fiber of indeterminate length. It is spun in many deniers, with its diameter varying from 10 to 50 μm. The cross section usually is round, trilobal, or square with hollow channels when used as carpet fiber.

Polyester. Polyester is made by the polymerization reaction of a diol and a diester. The main commercial polymer is formed by a condensation reaction using ethylene glycol and terephthalic acid. Fibers are formed by melt-spinning. Commercially introduced in 1953 by the DuPont Company as Dacron, polyester fibers have high strength, and very low moisture absorbance. The fiber is usually spun with a round cross section. Polyester is the most used synthetic fiber around the world.

Acrylics. The DuPont Company introduced the first commercial acrylic fiber, Orlon, in 1950. Acrylics are made from the polymerization of acrylonitrile and other co-monomers to allow dyeability and to open the internal structure.

The fibers are produced by either solvent-spinning (Orlon), or wet-spinning (Acrilan). In the solvent-spinning process, the polymer is dissolved in a low-boiling liquid solvent such as dimethyl formamide and extruded in a warm air chamber. In wet-spinning, the polymer is dissolved in a suitable solvent, extruded into a coagulation bath, dried, crimped, and collected. Although the acrylic fibers are extruded as continuous filaments, they subsequently are cut into staple-length fibers. Acrylics have found a niche market as a substitute for wool or in wool blends (blankets, sweaters, etc.) and in awnings and boat covers. The cross section of the filament varies among manufacturers, Orlon having a dog-bone configuration and Acrilan having a lima-bean shape. Acrylic fibers are quick drying and wrinkle resistant.

Polyolefins. Polyolefin fibers are produced from the polymerization of ethylene or propylene gas. The catalysis research of Ziegler and Natta led to the development of these polymers to form crystalline polymers of high molecular weight. Hercules Inc. produced the first commercial fibers in 1961. The fibers made from these polymers are melt-spun. The cross sections are round, and the fibers are smooth. They have extremely low dye affinity and moisture absorbance. Colored fiber is normally produced by mixing pigments in the melt polymer prior to extrusion.

Elastane. The DuPont Company commercialized the first manufactured elastic fiber, Lycra, in 1958. Originally categorized as a spandex fiber, the name "elastane" has become more common around the world. This specialty fiber is described as segmented polyurethane that contains "hard" and "soft" segments; their ratio determines the amount of stretch built into the fiber. Elastane fibers are formed by dry-spinning or solvent-spinning. The continuous filaments can be coalesced multifilaments or monofilaments, depending on the manufacturer. Because most dyeings are applied from water solutions or dispersions, the effect of water absorption by the fiber is an important criterion. Table 4 shows the hydrophobic/hydrophilic characteristics of the important fibers. The cellulosic and natural fibers are the most hydrophilic, and polyolefin is the most hydrophobic.

Table 4 Hydrophobic/hydrophilic characteristics of various fibers

Fiber	Moisture content, % (at 65% R. H.−70 °F)	Water retention, % (weight change in water)	Swelling, % (volume change in water)
Acetate	6.5	20–25	NA
Acrylic	1.0–1.5	4.5–6	2
Cotton	7	45	45
Elastane	0.3–1.5	low	low
Nylon	3.0–5.0	9–12	13
Polyester	0.3–0.5	3–5	0.5
Olefin	0.01–0.1	Very low	Very low
Triacetate	3.2	12–18	NA
Viscose	13	90–100	95
Wool	13–15	42	42

Microdenier Fibers. The first commercial production of microfiber in the United States was in 1989 by the DuPont Company. Today microfibers are produced in a variety of synthetic fibers (i.e., polyester, nylon, acrylic). A microfiber is a fiber that is less than one denier per filament. Yarns made from microdenier filaments are able to give silklike hand to fabrics.

Classification of Dyes

Dyes can be classified according to their usage or application method or according to chemical structure. In this chapter, the dyes are classified according to their usage or application method such as acid, basic (cationic), direct, disperse, reactive, solvent, sulfur, and vat dyes. Classification by usage or application is the principal system adopted by the Colour Index (CI). Traditional chemical classes of dyes such as azo, anthraquinone, phthalocyanine, and triphenylmethane are also included. With regard to the application of synthetic dyes to textiles, it is well known that dyeing of textile fibers from an aqueous dye bath involves four steps: exhaustion, diffusion, migration, and fixation. In step 1, individual dye molecules move from the dye bath to the fiber surface and in step 2, dye molecules move from the fiber surface into the amorphous regions of the fiber. In step 3, dye molecules move from regions of high concentration to regions of low concentration (i.e., migrate) to become uniformly distributed within the polymer matrix. In step 4, dye molecules interact with groups along the polymer chain via primary or secondary valency forces. Dye-polymer interactions can involve ionic bonding (e.g., acid dyes on nylon or wool), covalent bonding (e.g., reactive dyes on cotton), mechanical entrapment (e.g., vat dyes and sulfur dyes on cotton), secondary valency forces (direct dyes on cotton), or solid–solid solution (e.g., disperse dyes on polyester).

Acid Dyes

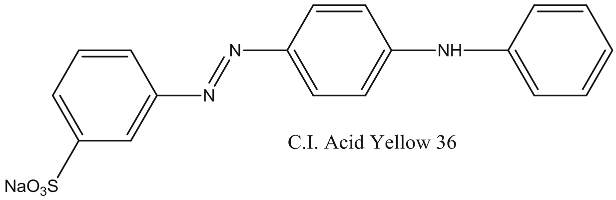
Acid dyes are used for dyeing polyamide, silk, and wool in the presence of an organic or inorganic acid (pH 2–6); hence they are called as acid dyes. Thus, the name “acid dye” is derived from the dyeing process. Acid dyes have sulfonic acid group, generally as sodium salt (R-SO_3Na). When dissolved in water, they produce colored anions (RSO_3^-) and colorless sodium cations (Na^+) [22].

Acid dyes are divided into three groups based on their differences in affinity (which is primarily a function of the molecular size), their application, and wet fastness properties:

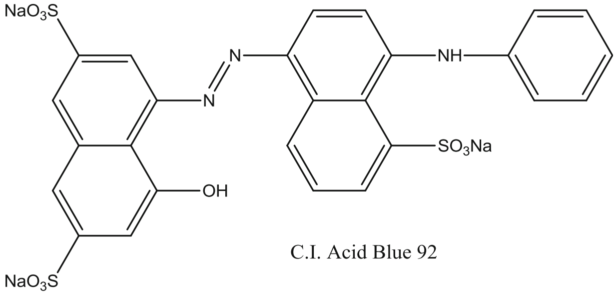
1. **Leveling Dyes** Leveling acid dyes level well and their fastness is generally good. Leveling dyes for wool have low molecular weights and usually require a highly acidic dye bath for good exhaustion.Leveling dyes for nylon have high molecular weights and are applied at a neutral or weakly acidic pH. Leveling dyes are relatively small molecules, which form a salt-like bond with the protein fiber.
2. **Milling Dyes** Milling acid dyes have better washing fastness than the leveling acid dyes but the shades generally lack brightness and good leveling power. Milling dyes are large-volume dye molecules, for which salt formation with fiber plays only a secondary role and the adsorption forces between the hydrophobic regions of the dye molecule and those of the protein fiber predominates.
3. **Super Milling Dyes** Super milling acid dyes are applied from neutral solutions. They are not level dyeing and their application requires considerable care because of their comparatively high molecular weights. Super milling dyes with intermediate molecular size not only form a salt-like bond with the wool fiber but are also bonded to the fiber by intermolecular forces and have properties lying in an intermediate position between those of the leveling and milling dyes. Chemically, acid dyes are divided into various subclasses such as nitro, nitroso, monoazo, diazo, azine, ketone-imine, quinolone, triphenylmethane, xanthine, and anthraquinone.

Acid Monoazo Dyes

Acid monoazo dyes exhibit brilliance of shades, very good leveling power, and low cost and are used for dyeing wool. The representative examples of acid monoazo dyes having aromatic amines as coupling components are C.I. Acid Yellow 36 and C.I. Acid Blue 92 as shown below.

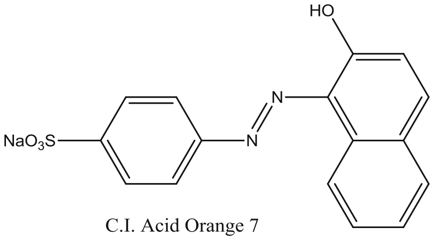


C.I. Acid Yellow 36

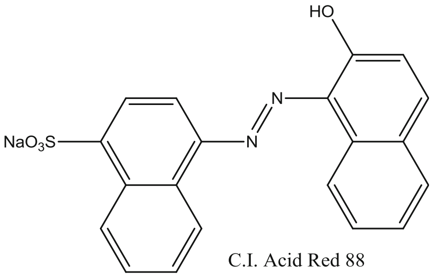


C.I. Acid Blue 92

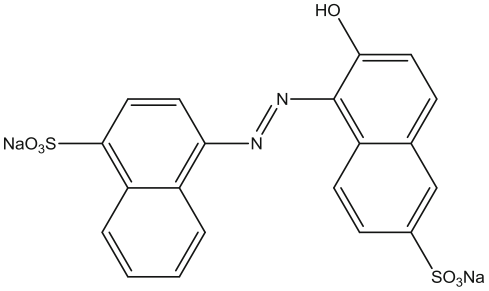
The representative examples of acid monoazo dyes having naphthols as coupling components are C.I. Acid Orange 7, C.I. Acid Red 88, and C.I. Acid Red 13 as shown below. C.I. Acid Orange 7 is a long-known, inexpensive acid monoazo dye and is used for dyeing wool, paper, and leather. C.I. Acid Red 88 and C.I. Acid Red 13 produce attractive red shades.



C.I. Acid Orange 7

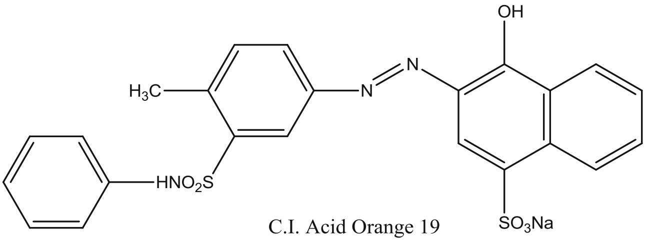


C.I. Acid Red 88

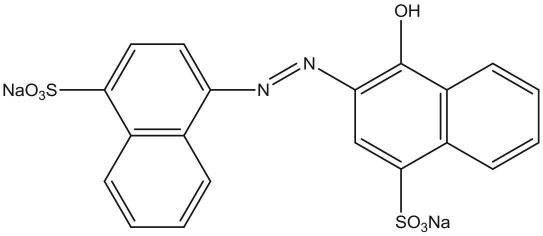


C.I. Acid Red 13

The representative examples of acid monoazo dyes having naphtholsulfonic acids as coupling components are C.I. Acid Orange 19 and C.I. Acid Red 14 as shown below. These dyes exhibit good fastness properties and are used for dyeing wool.

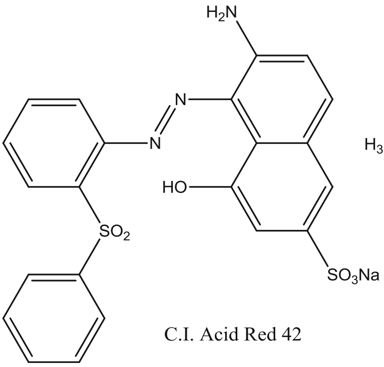


C.I. Acid Orange 19

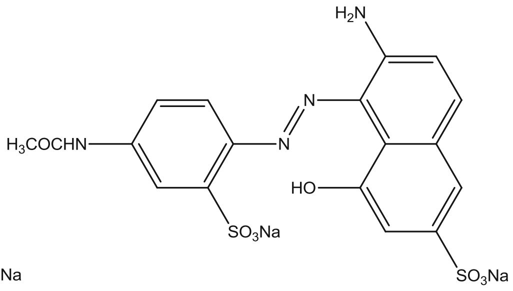


C.I. Acid Red 14

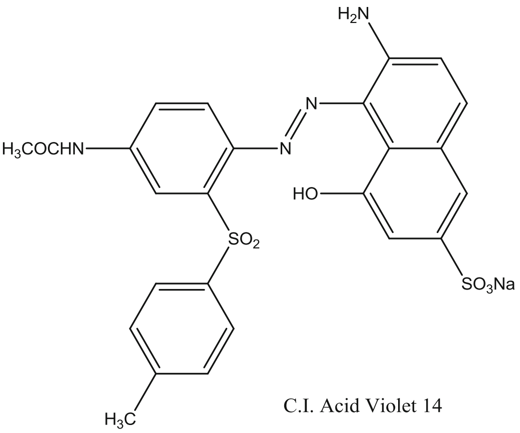
The representative examples of acid monoazo dyes having aminonaphtholsulfonic acids as coupling components are C.I. Acid Red 42, C.I. Acid Red 37, and C.I. Acid Violet 14 as shown below. These dyes show good light-fastness, wet-fastness, and good leveling power properties and are used for dyeing wool.



C.I. Acid Red 42

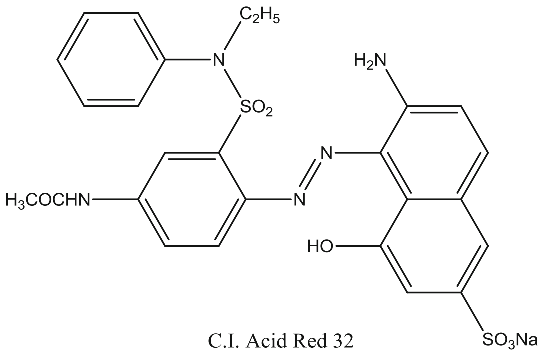


C.I. Acid Red 37

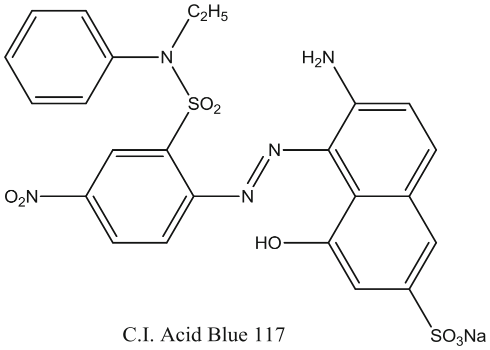


C.I. Acid Violet 14

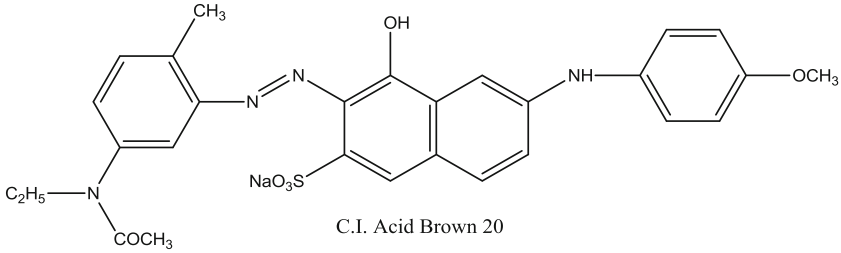
Further representative examples of acid monoazo dyes having aminonaphtholsulfonic acids as coupling components are C.I. Acid Red 32 and C.I. Acid Blue 117 as given below. These dyes exhibit very good wet-fastness and high leveling power properties and are used for dyeing wool. Another representative example of acid monoazo dye having aminonaphtholsulfonic acid as coupling components is C.I. Acid Brown 20 as shown below, which results in strong deepening shades and is used for dyeing silk and wool.



C.I. Acid Red 32

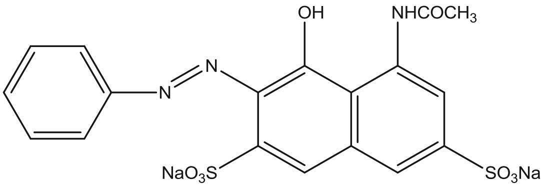


C.I. Acid Blue 117

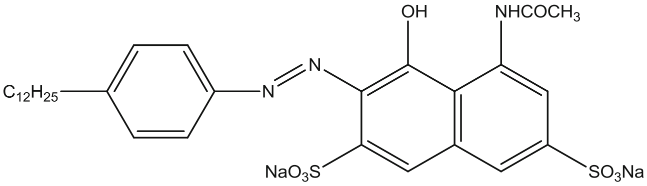


C.I. Acid Brown 20

Acylation of the amino group of coupling component aminonaphtholsulfonic acids substantially improves light-fastness, wet-fastness, and leveling power. The representative examples of acid monoazo dyes having acylaminonaphtholsulfonic acids as coupling components are C.I. Acid Red 1 and C.I. Acid Red 138 as shown below. Incorporating long-chain hydrophobic hydrocarbon radical in C.I. Acid Red 138 results in very good wet-fastness properties and neutral affinity to wool.

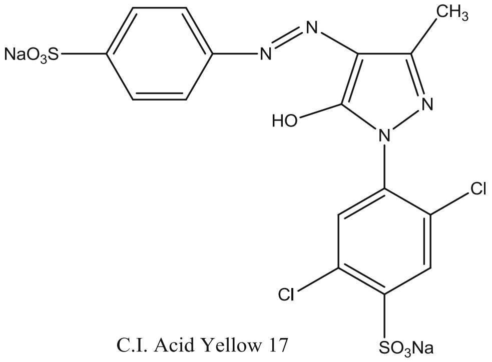


C.I. Acid Red 1

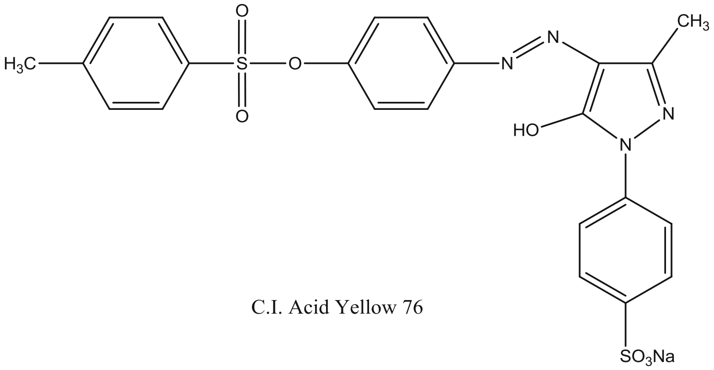


C.I. Acid Red 138

Light-fast yellow shades can especially be achieved by using 1-phenyl-5-hydroxypyrazole as coupling components. 1-Aryl-3-methyl-5-hydroxypyrazole is preferred over corresponding 3-carboxy-5-hydroxypyrazole due to cost. These series generate a wide range of possible variations that the dyes extend from greenish yellow to reddish orange. The representative examples of acid monoazo dyes having 1-phenyl-5-hydroxypyrazole as coupling components are C.I. Acid Yellow 17 and C.I. Acid Yellow 76 as shown below. These dyes show good light-fastness and good milling-fastness properties and yield a clear, superbly light-fast yellow on wool.



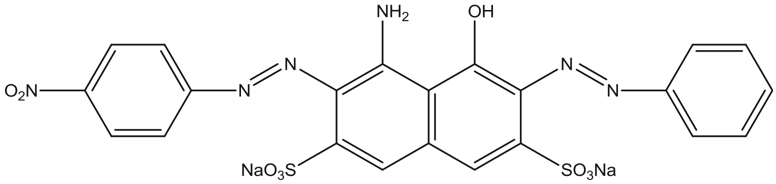
C.I. Acid Yellow 17



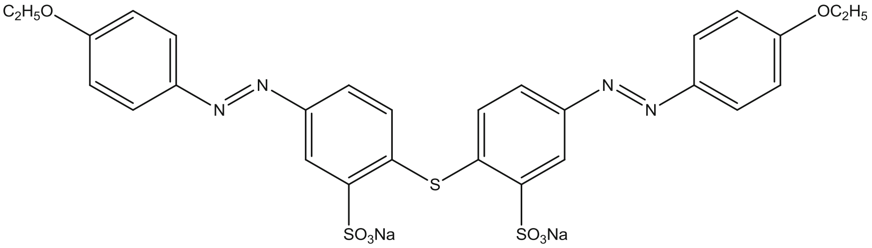
C.I. Acid Yellow 76

Acid Disazo Dyes

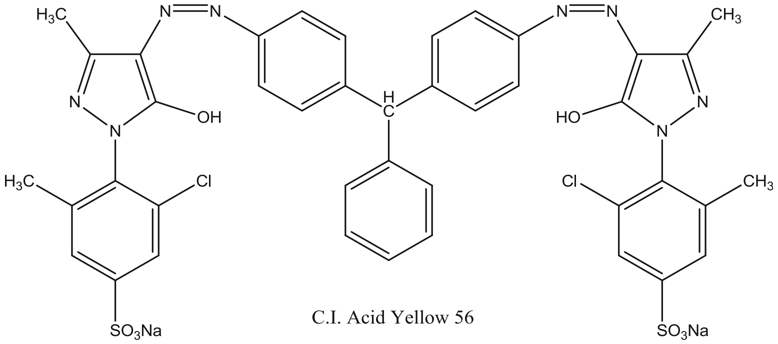
Acid disazo dyes contain two azo groups. One of the most important representative examples of acid disazo dye is C.I. Acid Black 1 as given below. It exhibits good light-fastness, high affinity, good leveling power but moderate wet-fastness. It dyes wool in blue-black shades. Another representative example of acid disazo dye is C.I. Acid Yellow 38 as given below. It particularly provides excellent milling-fatness and dyes wool in bright yellow shades. Further representative example of acid disazo dye is C.I. Acid Yellow 56 as given below. It demonstrates good light-fastness, excellent wet-fastness, and usually neutral dyeing on wool.



C.I. Acid Black 1

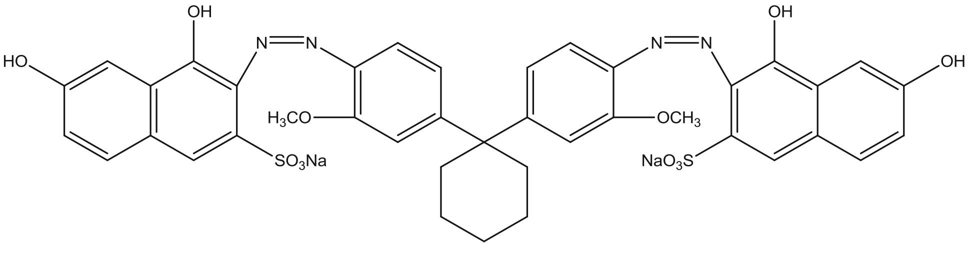


C.I. Acid Yellow 38

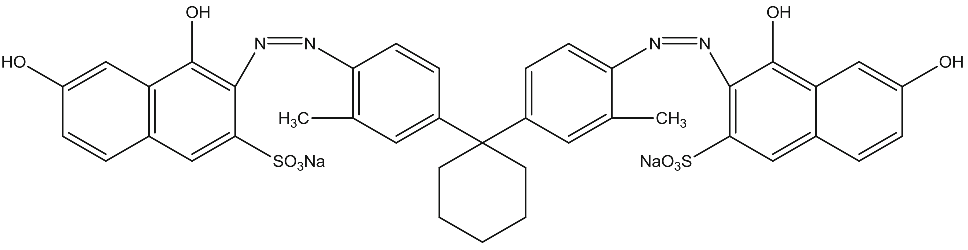


C.I. Acid Yellow 56

Additional representative examples of acid disazo dyes are C.I. Acid Red 134 and C.I. Acid Red 154 as shown below. These dyes are used for dyeing polyamide and wool.

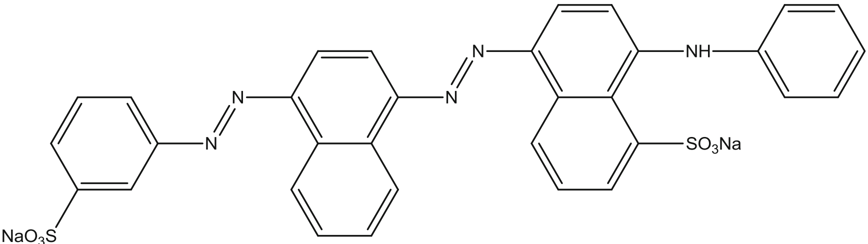


C.I. Acid Red 134

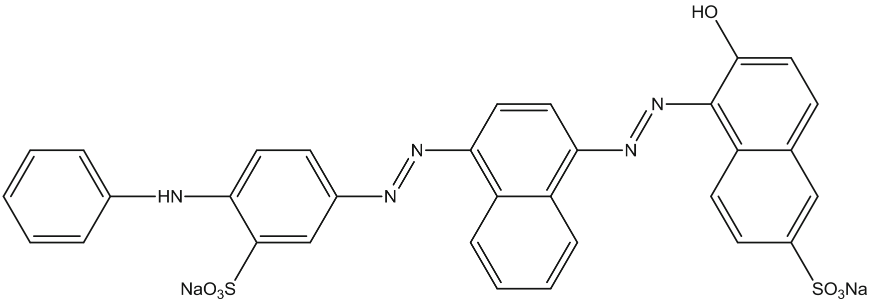


C.I. Acid Red 154

Further representative examples of acid disazo dyes are C.I. Black 24 and C.I. Acid Black 26 as shown below. These dyes give high yield, show very good wash-fastness and light-fastness, and are used for dyeing wool.



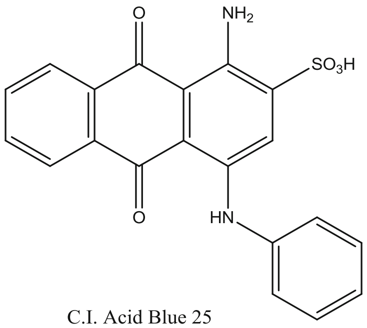
C.I. Acid Black 24

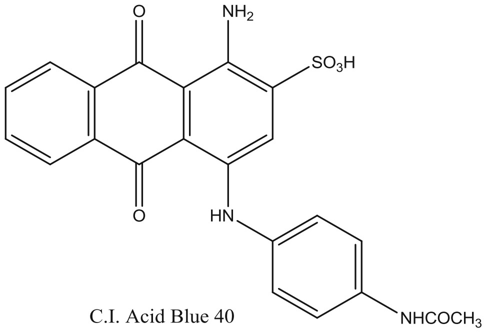


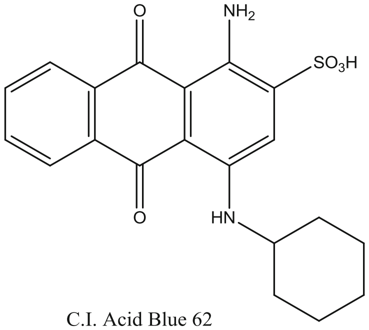
C.I. Acid Black 26

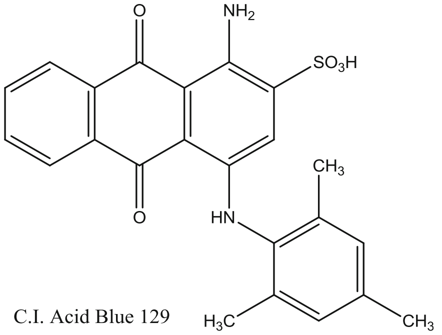
Acid Anthraquinone Dyes

Red and yellow acid anthraquinone dyes are of little importance. The majority of the commercially available acid anthraquinone dyes give bright blue shades as these are not obtained by azo dyes. Dyes of green shades can be achieved by combining blue and yellow dyes. The uniformly dyeing green dyes of the acid anthraquinone series are of special value. Acid anthraquinone dyes can be classified for particular applications according to their light-fastness, wash-fastness, and leveling characteristics. The representative examples of acid anthraquinone dyes containing 1-aminoanthraquinone-2-sulfonic acid are C.I. Acid Blue 25, C.I. Acid Blue 40, C.I. Acid Blue 62, and C.I. Acid Blue 129 as shown below.

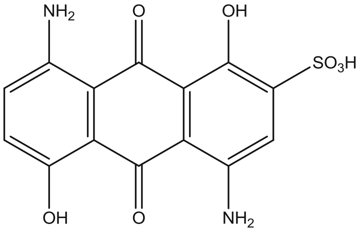

C.I. Acid Blue 25


C.I. Acid Blue 40

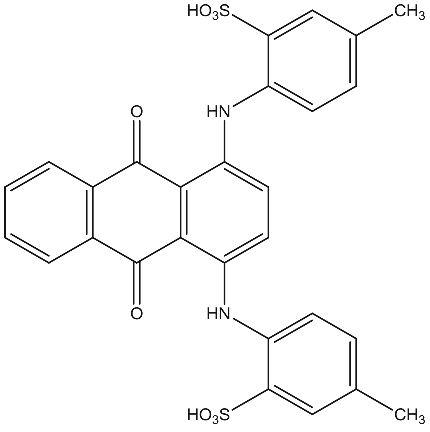

C.I. Acid Blue 62

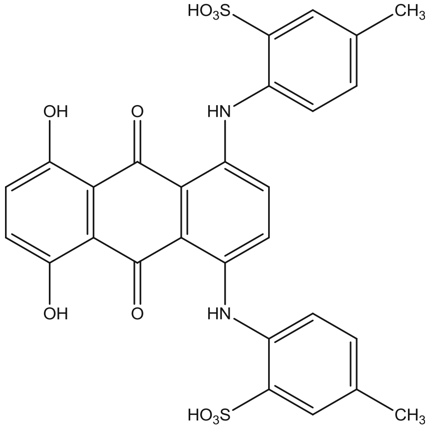

C.I. Acid Blue 129

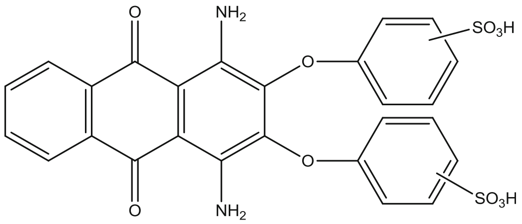
The representative example of acid anthraquinone dyes containing diaminodihydroxyanthraquinone sulfonic acids for dyeing wool is C.I. Acid Blue 43 as shown below.


C.I. Acid Blue 43

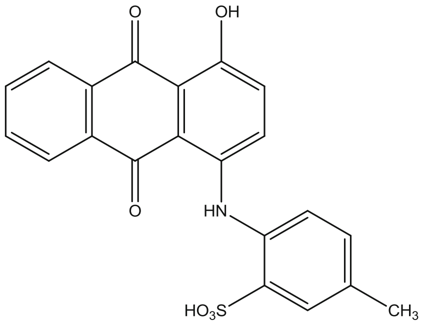
The representative examples of acid anthraquinone dyes containing 1,4-diaminoanthraquinones with external sulfonic acid groups are C.I. Acid Green 25, C.I. Acid Green 41, and C.I. Acid Violet 42 as shown below. Further representative example of acid anthraquinone dyes containing 1-amino-4-hydroxyanthraquinones with external sulfonic acid groups is C.I. Acid Violet 43 as shown below.


C.I. Acid Green 25


C.I. Acid Green 41



C.I. Acid Violet 42



C.I. Acid Violet 43

Basic Dyes

Basic dyes are ionic dyes in which the colored part of the molecule is positively charged (cationic). For this reason, they are frequently referred as cationic dyes. They have good solubility in water. Basic dyes have high colored value and are among the brightest dyes available. Historically, basic dyes are important because the first synthetic dye, Mauve, synthesized by Perkin in 1856, is a basic dye. They have good fastness properties at a reasonable price. Basic dyes are applied to fibers made up of negatively charged polymer molecules. Bonds can be formed between the cation of the dye molecule and the anionic site in the fiber. Basic dyes are applied to cotton, silk, wool, acrylic fibers, paper, plastics, leather, and waxes [23–26].

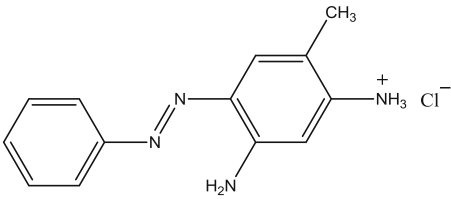
In general, there are two important groups of cationic dyes:

1. Localized or pendant cationic dyes: Those in which the positive charge is localized on one atom, usually a nitrogen atom.
2. Delocalized cationic dyes: Those in which the positive charge is delocalized over the entire molecule (chromogen).

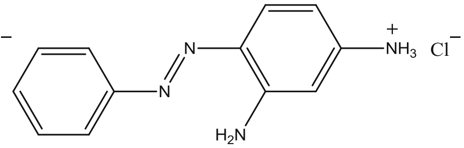
Localized or Pendant Cationic (Basic) Dyes

This group includes azo and anthraquinone dyes used for polyacrylonitrile fibers by the introduction of a pendant cationic group. These dyes are bright and show tinctorial strength.

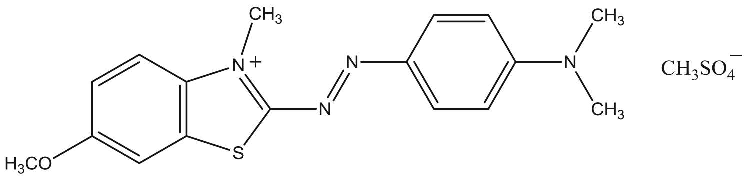
The representative examples of localized or pendant cationic (basic) dyes are C.I. Basic Orange 1, C.I. Basic Orange 2, C.I. Basic Blue 54, and C.I. Basic Blue 22 as shown below.



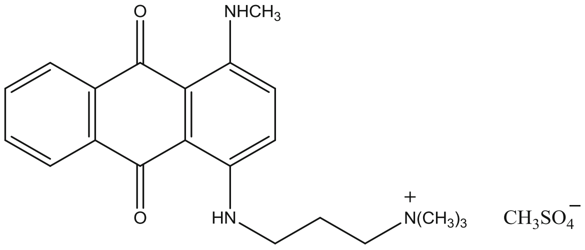
C.I. Basic Orange 1



C.I. Basic Orange 2



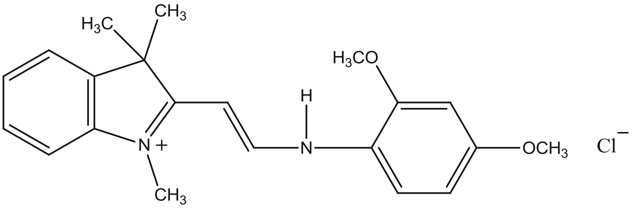
C.I. Basic Blue 54



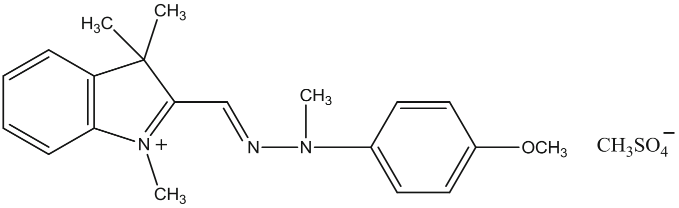
C.I. Basic Blue 22

Delocalized Cationic (Basic) Dyes

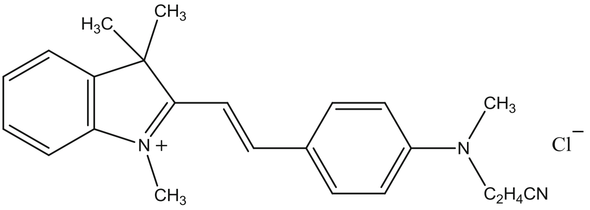
This group includes polymethine, triphenylmethane, oxazine, and thiazine (and their heterocyclic analogs) dyes. These dyes show exceptionally high tinctorial strength, high brightness, high fastness properties, and improved cost-effectiveness. The representative examples of delocalized cationic (basic) dyes are C.I. Basic Yellow 11, C.I. Basic Yellow 28, C.I. Basic Red 14, and C.I. Basic Blue 3 as shown below.



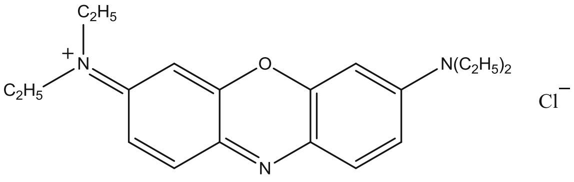
C.I. Basic Yellow 11



C.I. Basic Yellow 28



C.I. Basic Red 14



C.I. Basic Blue 3

Direct Dyes

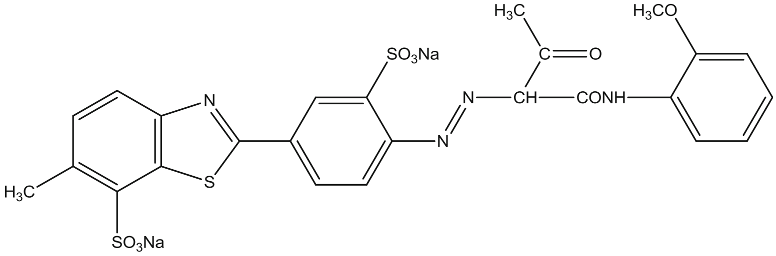
This class of dyes is called direct dyes because they dye cellulosic fibers *directly* without mordanting, which was necessary when trying to dye cellulosics with virtually all naturally occurring dyes. The first direct dye of this family was reported in 1884 and is called Congo red. Direct or substantive dyes are water-soluble anionic dyes, which when dyed from aqueous solution in the presence of electrolytes are substantive, i.e., have affinity for cellulosic fibers (cotton, viscose rayon, jute, hemp, linen, and ramie) [22, 27].

Direct dyes provide the simplest means of coloring cellulosic materials since they are normally applied from a neutral to slightly alkaline bath, at or near the boil, to which sodium chloride or sulfate is added in such quantities and at such intervals of time appropriate to the dyeing properties of individual dyes. The essential requirement of a dye in this group is its substantivity, i.e., its absorption from an aqueous salt-containing solution onto cellulosic materials. Absorption onto cotton takes place in a neutral or an alkaline medium and onto paper in a weakly acidic or neutral medium. The principal use of these dyes is the dyeing of cotton and regenerated cellulose, paper, leather, wool, silk, and to a lesser extent nylon. They are also used as pigments, indicators, and biological stains. Because of their ease of application and moderate price, direct dyes still represent one of the largest groups of azo dyes, although they have limited wet-fastness.

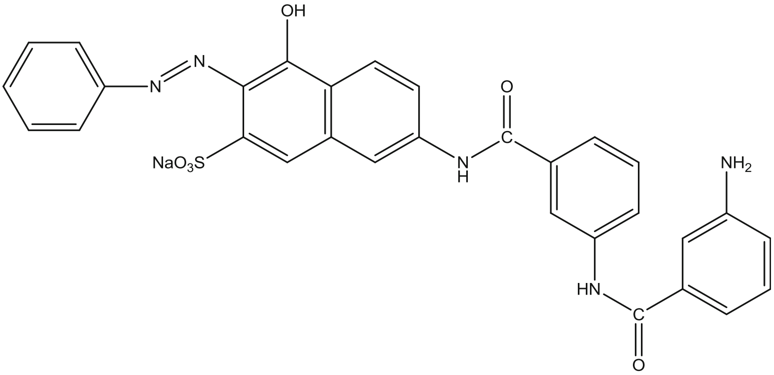
The majority of direct dyes belong to dis-, tris-, and polyazo classes, the remainder being monoazo, oxazine, stilbene, thiazole, triazine, and phthalocyanine compounds.

Direct Monoazo Dyes

The representative examples of direct monoazo dyes are C.I. Direct Yellow 27 and C.I. Direct Orange 75 as shown below.



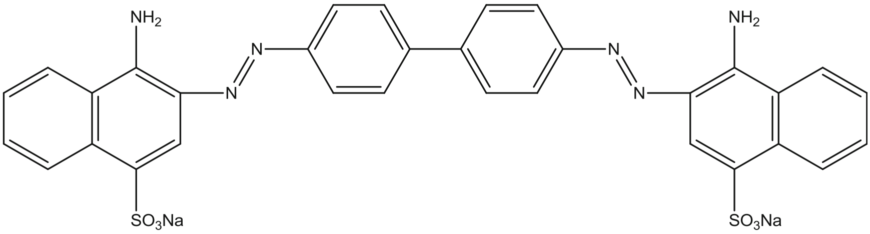
C.I. Direct Yellow 27



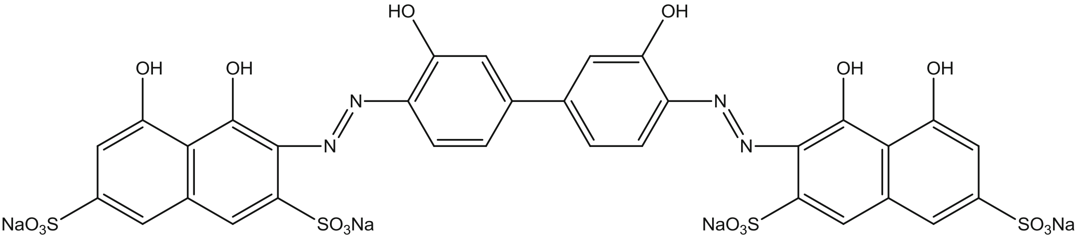
C.I. Direct Orange 75

Direct Disazo Dyes

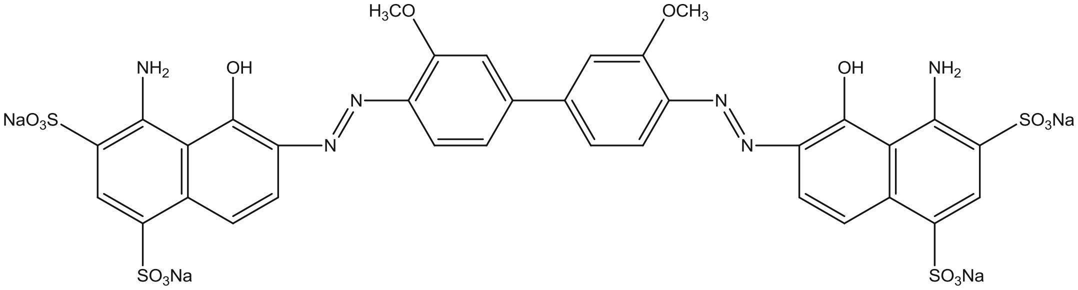
The representative examples of direct disazo dyes containing benzidine nucleus are C.I. Direct Red 28, C.I. Direct Blue 84, and C.I. Direct Blue 1 as shown below.



C.I. Direct Red 28 (Congo Red)

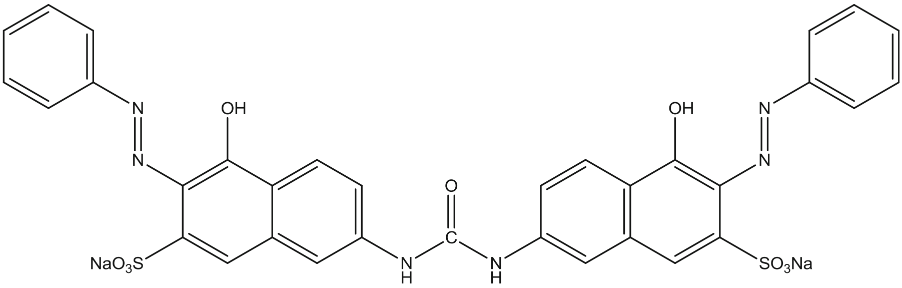


C.I. Direct Blue 84

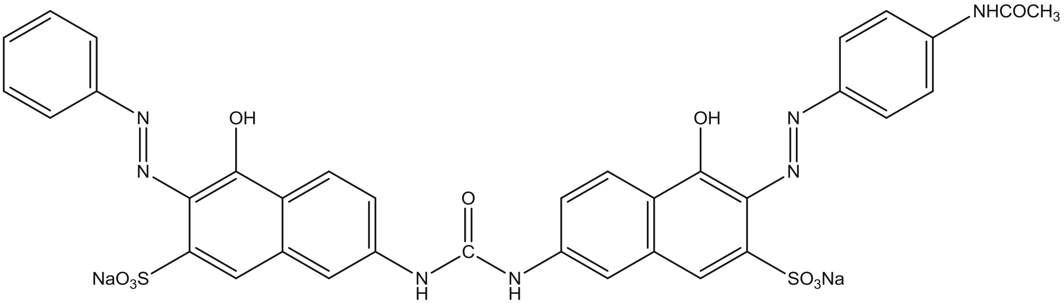


C.I. Direct Blue 1

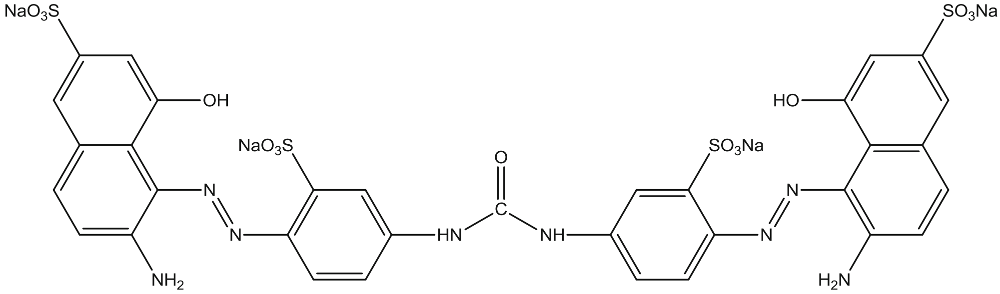
The representative examples of direct disazo dyes containing a urea bridge are C.I. Direct Orange 26, C.I. Direct Red 23, and C.I. Direct Red 75 as shown below. The urea bridge increases the substantivity of the dyes.



C.I. Direct Orange 26



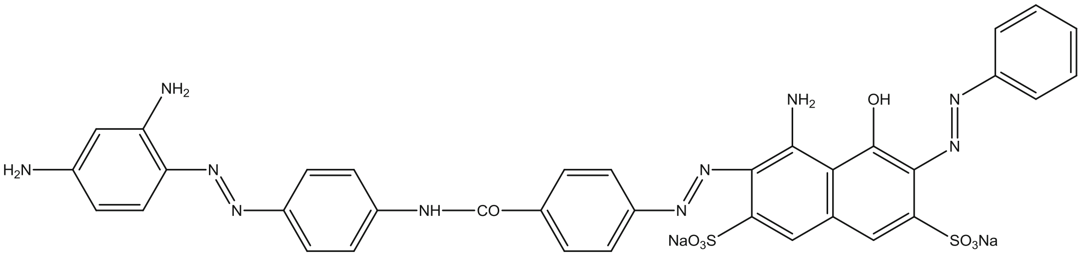
C.I. Direct Red 23



C.I. Direct Red 75

Direct Trisazo Dyes

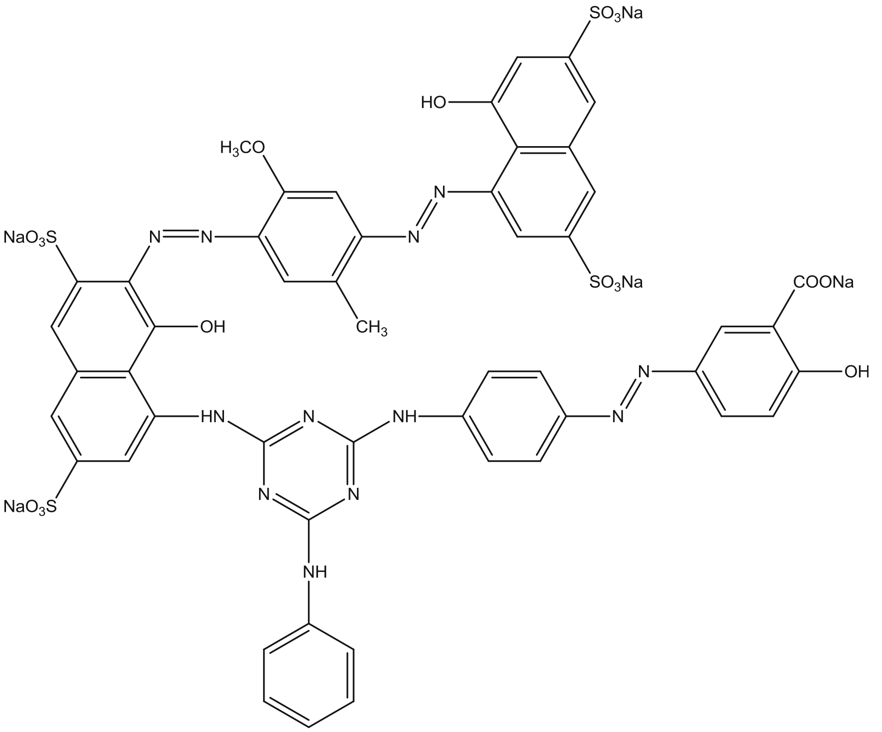
The trisazo dyes include in particular blue, green, and black shades. The representative example of direct trisazo dye is C.I. Direct Black 166 as shown below.



C.I. Direct Black 166

Direct Triazinyl Dyes

The direct triazinyl dyes include a triazine ring as a bridge to link two separate chromophoric systems. The triazine bridge increases the substantivity of the dyes, similar to urea group. The representative example of direct triazinyl dye is C.I. Direct Green 26 as shown below.



C.I. Direct Green 26

Disperse Dyes

Disperse dyes are substantially water insoluble, colloidally dispersed, nonionic dyes for application to hydrophobic fibers from aqueous dispersion. These dyes are used predominantly on polyesters and to a lesser extent on acrylic, cellulose, cellulose acetate, and nylon fibers. When the dye is applied from the aqueous medium, it is adsorbed from the molecularly dispersed aqueous solution onto the fiber surface and then diffuses into the interior of the fiber [28–31].

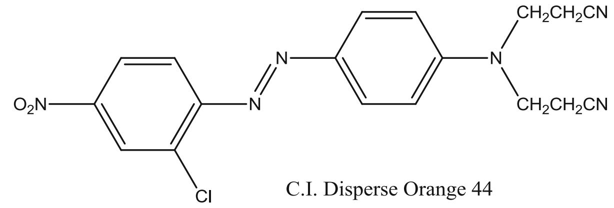
Chemically, disperse dyes are classified based on various chromophores such as azo, anthraquinone, quinaphthalone, methane, and nitro dyes.

Disperse Azo Dyes

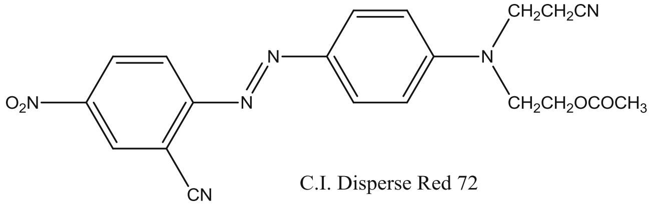
Disperse azo dyes represent the largest group of disperse dyes because of the relatively simple process by which the dyes are produced and the ease with which an extraordinary number of combinations can be generated by varying the diazo and coupling components. Disperse azo dyes can be further divided into monoazo dyes and disazo dyes.

Disperse Monoazo Dyes

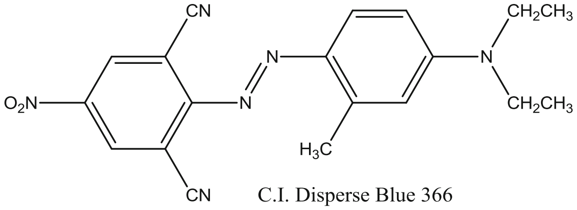
Disperse monoazo dyes derived from aromatic amines as coupling components and carbocyclic aromatic amines as diazo components are of greatest economic importance. The representative examples of disperse monoazo dyes derived from aromatic amines as coupling components and carbocyclic aromatic amines as diazo components are C.I. Disperse Orange 44, C.I. Disperse Red 72, C.I. Disperse Blue 366, and C.I. Disperse Blue 165 as shown below and are used for dyeing polyester.



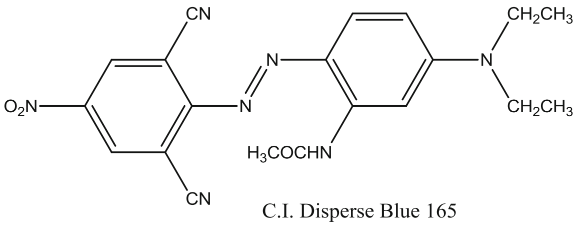
C.I. Disperse Orange 44



C.I. Disperse Red 72

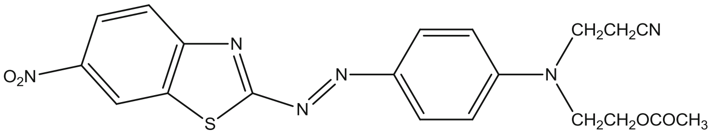


C.I. Disperse Blue 366

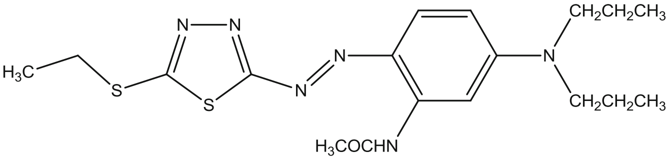


C.I. Disperse Blue 165

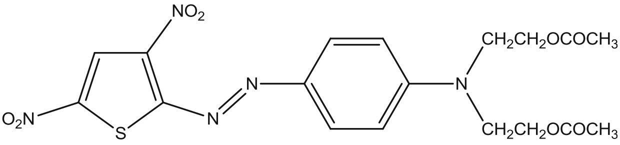
Disperse monoazo dyes derived from heterocyclic amines as diazo components represent an important class of bright dyes. The representative examples of disperse monoazo dyes derived from heterocyclic amines as diazo components are C.I. Disperse Red 177 (with thiazole heterocycle as diazo component), C.I. Disperse Red 338 (with thiadiazole heterocycle as diazo component), C.I. Disperse Blue 284 (with thiophene heterocycle as diazo component), and C.I. Disperse Green 9 (with thiophene heterocycle as diazo component) as shown below and are used for dyeing polyester. The greatest commercial success achieved in the field of dyestuffs from Gewald chemistry is the synthesis of C.I. Disperse Blue 284 and C.I. Disperse Green 9 [32].



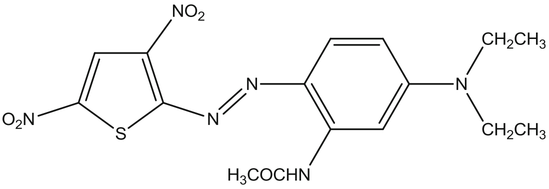
C.I. Disperse Red 177



C.I. Disperse Red 338

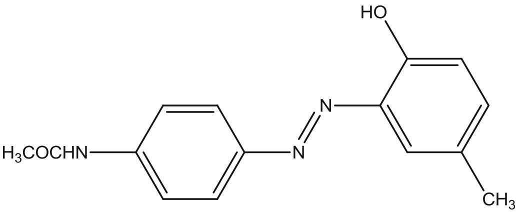


C.I. Disperse Blue 284



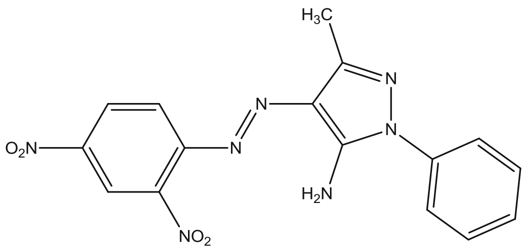
C.I. Disperse Green 9

Disperse monoazo dyes derived from aromatic hydroxy compounds as coupling components are used for dyeing acetate and polyester fibers. The representative example of disperse monoazo dye derived from aromatic hydroxy compound as coupling component is C.I. Disperse Yellow 3 as shown below.

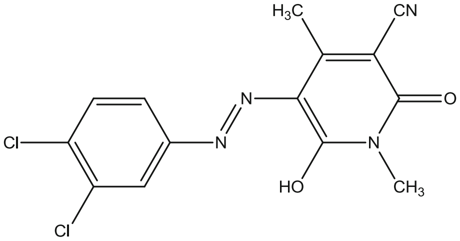


C.I. Disperse Yellow 3

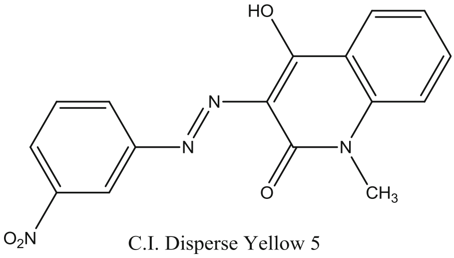
Disperse monoazo dyes derived from heterocyclic compounds as coupling components are used for dyeing acetate fibers. The representative examples of disperse monoazo dyes derived from heterocyclic compounds as coupling component are C.I. Disperse Orange 56 (with pyrazole heterocycle as coupling component), C.I. Disperse Yellow 241 (with pyridine heterocycle as coupling component), and C.I. Disperse Yellow 5 (with quinoline heterocycle as coupling component) as shown below.



C.I. Disperse Orange 56



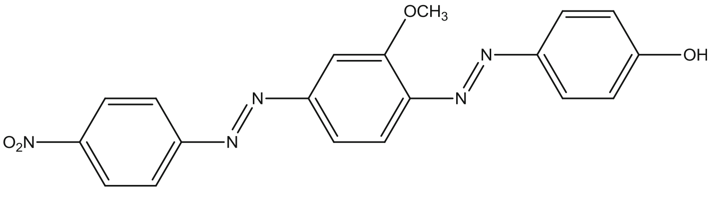
C.I. Disperse Yellow 241



C.I. Disperse Yellow 5

Disperse Disazo Dyes

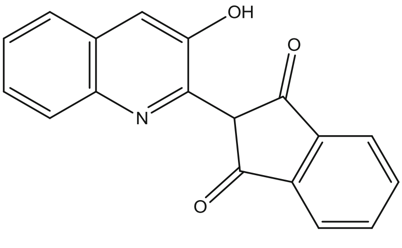
Disperse disazo dyes derived from aromatic amines as coupling components and phenols as diazo components are simplest disazo dyes. The representative example of disperse disazo dye derived from aromatic amine as coupling component and phenolic compound as diazo component is C.I. Disperse Orange 29 as shown below. The introduction of an alkoxy group into the central benzene ring causes a distinct shift towards orange. Substitution of the first benzene nucleus by electron acceptor also causes bathochromic shifts. This dye has good affinity for polyester fibers and yield lightfast reddish yellow hues.



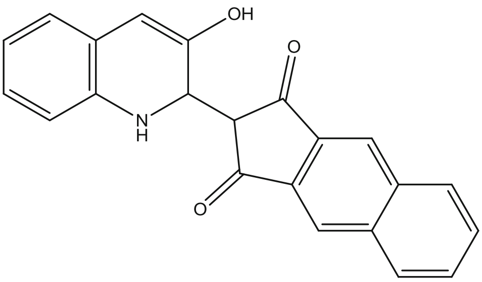
C.I. Disperse Orange 29

Disperse Quinophthalone Dyes

Disperse quinophthalone dyes are extensively used for dyeing synthetic fibers. These dyes have good light-fastness and moderate to good sublimation-fastness and produce greenish yellow hues. Suitable substitution in quinolone nucleus or phthalic anhydride residue improves thermosetting fastness. The representative examples of disperse quinophthalone dyes are C.I. Disperse Yellow 54 and C.I. Disperse Yellow 160 as shown below.



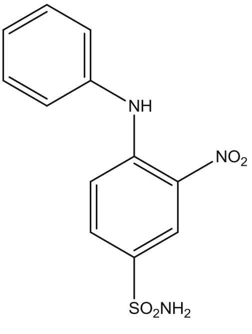
C.I. Disperse Yellow 54



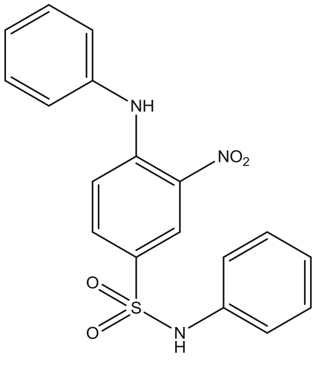
C.I. Disperse Yellow 160

Disperse Nitro Dyes

These dyes contain an aromatic nucleus with a nitro group (–NO_2) in the *ortho*-position to an electron-donating substituent, usually NH_2. Nitro dyes are deeply yellow or dirty yellow to brown colored. Due to their relatively small molecular size, these dyes became important dyes for dyeing polyester fibers. Nitrodiphenylamine dyes have retained a niche in the armory of dyes available for polyester coloration, principally because of their ability to produce yellow shades of very high light-fastness on the fiber. The dyes of particular interest on polyester also have a sulfonamide substituent *para* to the amine in the ring containing the nitro group. The nitro substituent is always found *ortho* to the amine because this forms the part of chromophoric system and results in improved light-fastness. The representative examples of disperse nitro dyes are C.I. Disperse Yellow 33 and C.I. Disperse Yellow 42 as shown below.



C.I. Disperse Yellow 33



C.I. Disperse Yellow 42

Disperse Anthraquinone Dyes

Disperse anthraquinone dyes, containing amino or hydroxyl functions, are major auxochromes, which produce brilliant red to blue shades. Yellow and orange shades are obtained by other dye classes. Choosing appropriate substituents on the anthraquinone nucleus determines which color is produced and allows the best dyes for various fibers.

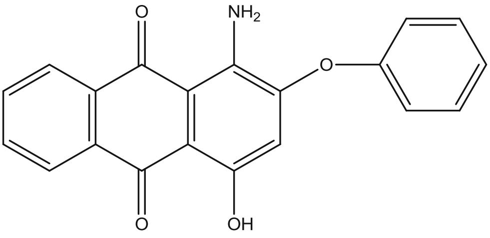
Disperse Anthraquinone Dyes for Polyester Fibers

1-Amino-4-hydroxyanthraquinones are bright red dyes, whose brilliance can be improved significantly by introduction of the ether group(s) ortho to amino group. Additional substituent in the side chains may improve sublimation-fastness. The representative example of disperse anthraquinone dye derived from 1-amino-4-hydroxyanthraquinone is C.I. Disperse Red 60 as shown below.

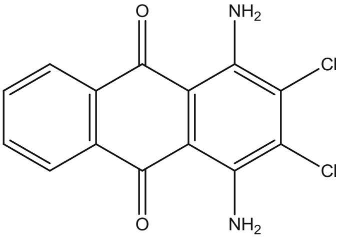
Disperse anthraquinone dyes derived from 1,4-diaminoanthraquinones generally show poor light-fastness; however, introduction of chlorine atoms into the β-position considerably improves light-fastness with little or no effect on sublimation-fastness. The representative example of disperse anthraquinone dye derived from 1,4-diaminoanthraquinones is C.I. Disperse Violet 28 as shown below.

Disperse anthraquinone dyes derived from N-alkyl- or N-arylaminohydroxy-anthraquinones demonstrate good affinity and light-fastness and produce yellow to blue shades. The representative examples of disperse anthraquinone dyes derived from N-alkyl- or N-arylaminohydroxyanthraquinones are C.I. Disperse Blue 27 and C.I. Disperse Blue 72 as shown below.

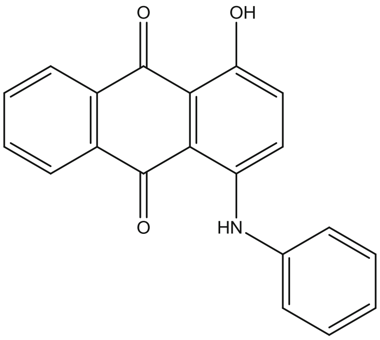
Disperse anthraquinone dyes derived from diaminodihydroxyanthraquinones are the most important disperse dyes with respect to affinity and shade. The dye properties can be optimized by introducing suitable substituents, selecting the positions of the isomers and blending. The representative example of disperse anthraquinone dye derived from diaminodihydroxyanthraquinone is C.I. Disperse Blue 73 as shown below.



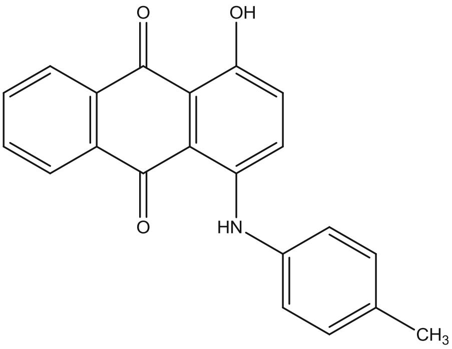
C.I. Disperse Red 60



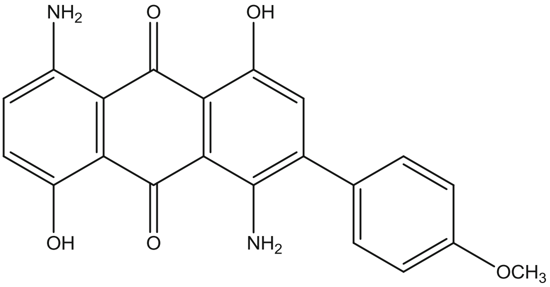
C.I. Disperse Violet 28



C.I. Disperse Blue 27



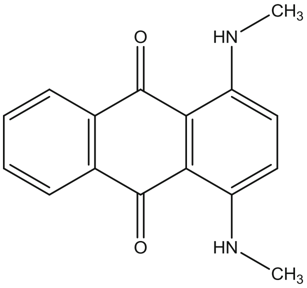
C.I. Disperse Blue 72



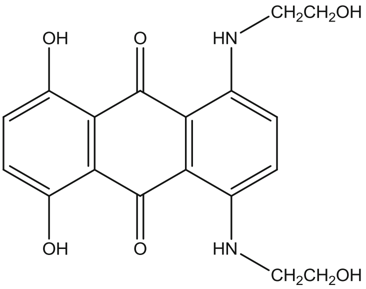
C.I. Disperse Blue 73

Disperse Anthraquinone Dyes for Cellulose Esters and Synthetic Polyamide Fibers

These were the first disperse dyes developed for dyeing cellulose fibers but their importance diminished considerably, when other synthetic fibers appeared on the market. Requirements regarding sublimation-fastness are not as stringent, whereas fastness to exhaust gases, ozone, and washing is important. Substitution of amino, especially alkylamino, does not decrease light-fastness for cellulose acetate and polyamide fibers. The representative examples of disperse anthraquinone dyes for cellulose esters and synthetic polyamide fibers are C.I. Disperse Blue 14 and C.I. Disperse Blue 7 as shown below.

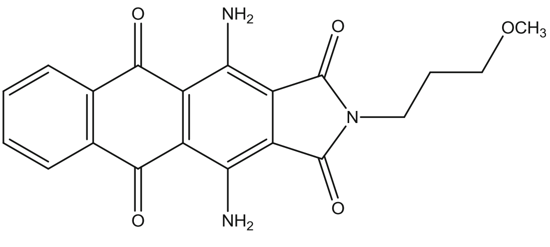


C.I. Disperse Blue 14

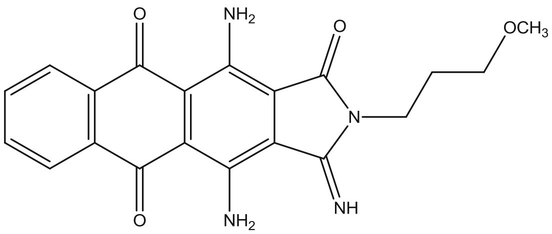


C.I. Disperse Blue 7

Further representative examples of disperse anthraquinone dyes for cellulose acetate and polyethylene terephthalate fibers are C.I. Disperse Blue 60 and C.I. Disperse Blue 87 as shown below.



C.I. Disperse Blue 60



C.I. Disperse Blue 87

Reactive Dyes

Reactive dyes are colored compounds which contain one or two groups capable of forming a covalent bond between the dye molecule and the given substrate (the fiber). The covalent bond is being formed between a carbon atom of the dye molecule and oxygen, nitrogen, or sulfur atom of the substrates, corresponding to hydroxyl, amino, or mercapto group of the substrate (fiber). Reactive dyes are mainly used for cotton but are also used to a small extent for wool and nylon. Marked advantages of reactive dyes over direct dyes are that their chemical structures are much simpler, their absorption spectra show narrower absorption bands, and their dyeings are brighter [33–44].

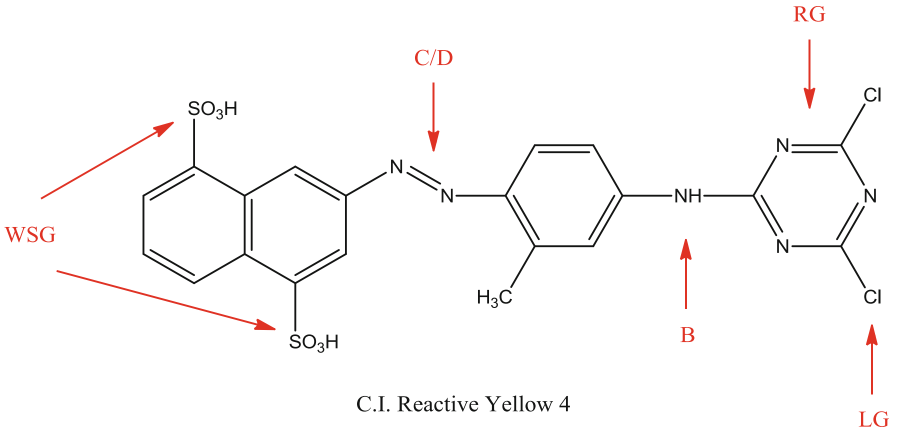
Reactive dyes contain one or more water-solubilizing groups (WSG), chromogen/dye (C/D), bridge or linker (B), reactive group (s) (RG), and a leaving group (LG). The schematic constitution of a reactive dye is shown in Fig. 1.

The schematic representation of each group of a reactive dye is shown in Fig. 2.

The representative examples of reactive groups (RG) in reactive dyes are dichlorotriazine, monochlorotriazine, trichloropyrimidine, dichloropyrimidine, dichloroquinoxaline, dichlorophthalazine, and chlorobenzothiazole as shown below.

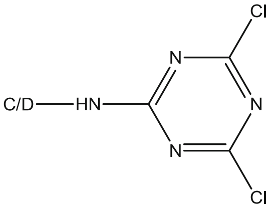
WSG——C/D——B——RG——LG

Fig. 1 Schematic constitution of a reactive dye

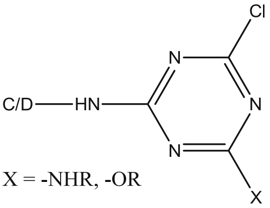


C.I. Reactive Yellow 4

Fig. 2 Schematic representation of each group of a reactive dye

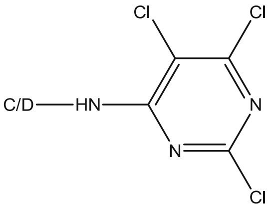


Dichlorotriazine

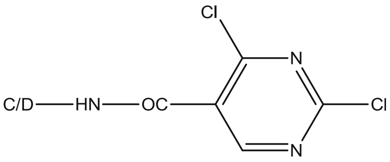


X = -NHR, -OR

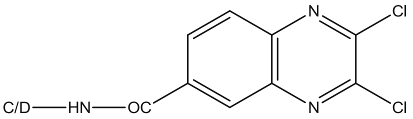
Monochlorotriazine



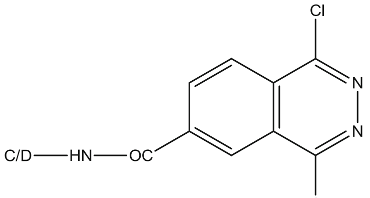
Trichloropyrimidine



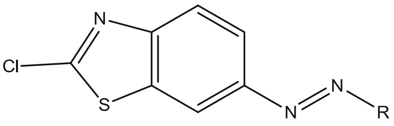
Dichloropyrimidine



Dichloroquinoxaline



Dichlorophthalazine



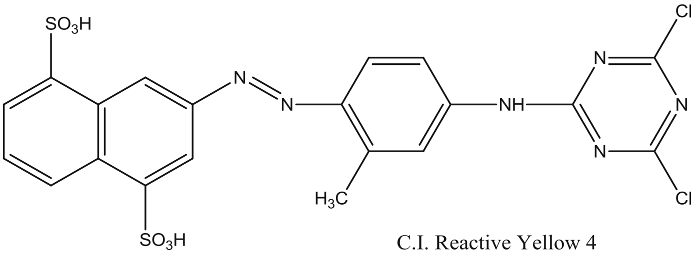
Chlorobenzothiazole

The leaving groups (LG) are F, Cl, and Br. The bridge or linker (B) groups must be sufficiently stable under acidic and/or basic reaction conditions. The bridge or linkers between the chromogen or dye and the reactive group are NH, NCH_3, and benzene-1,4-diamino bridge. The dyes or chromogens are suited for dyeing. The dye or chromogen creates yellow, orange, red, violet, ruby, and blue colors. The water-solubilizing groups are sulfonic acids.

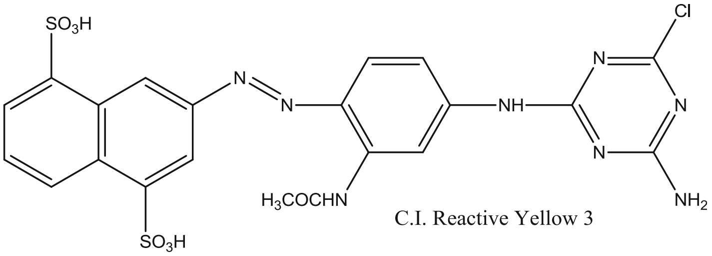
The chemical classes of the reactive dyes are azo (including metalized azo), triphenodioxazine, phthalocyanine, formazan, and anthraquinone.

Reactive Azo Dyes

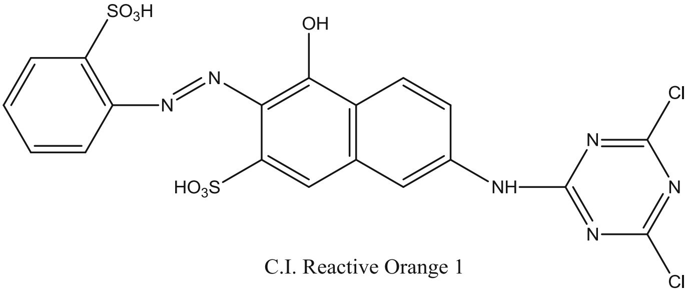
Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) is a molecule of wide synthetic potential because the three chlorine atoms on the triazine ring differ in their reactivities. The first chlorine atom exchanges with nucleophiles in water at 0–5 °C, the second at 35–40 °C, and the third at 80–85 °C. A wide variety of triazinyl dyes can be synthesized by careful selection of the reaction conditions. The representative examples of reactive azo dyes are C.I. Reactive Yellow 4, C.I. Reactive Yellow 3, C.I. Reactive Orange 1, and C.I. Reactive Red 12 as shown below.



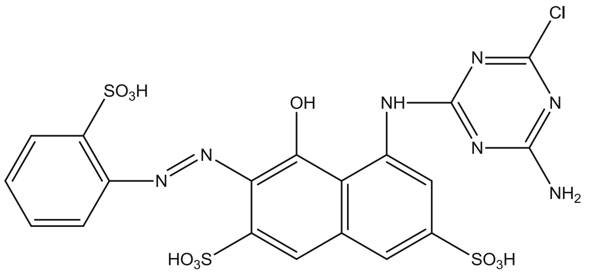
C.I. Reactive Yellow 4



C.I. Reactive Yellow 3



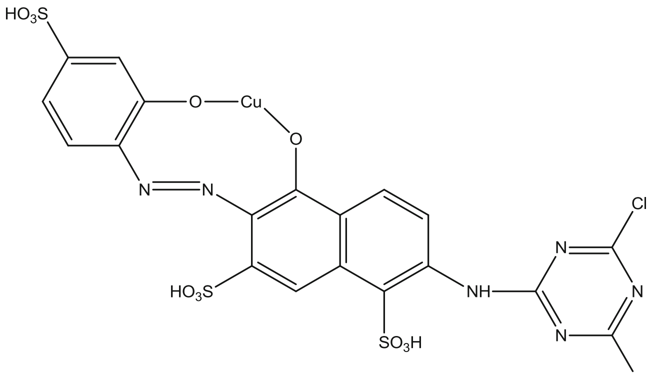
C.I. Reactive Orange 1



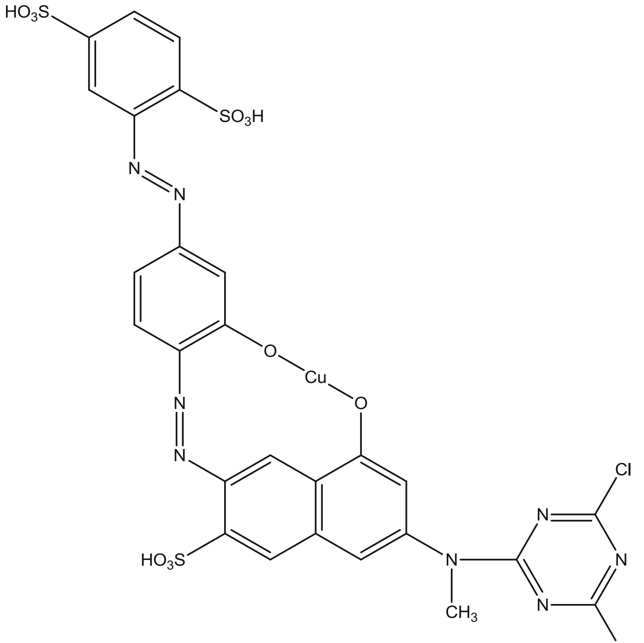
C.I. Reactive Red 12

Reactive Metal Complex Azo Dyes

Exceptionally lightfast colors are obtained with metal-complexed azo dyes. The representative examples of reactive metal complex azo dyes are C.I. Reactive Red 6 and C.I. Reactive Blue 40 as shown below.



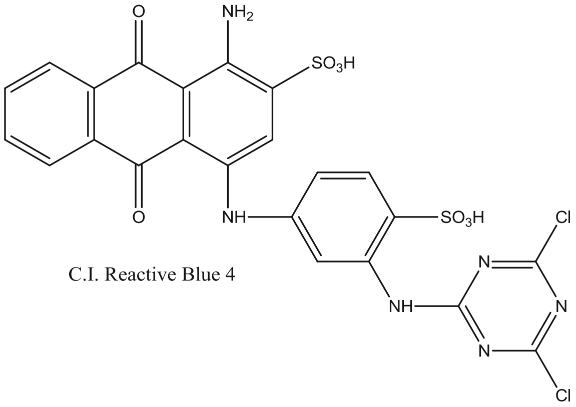
C.I. Reactive Red 6

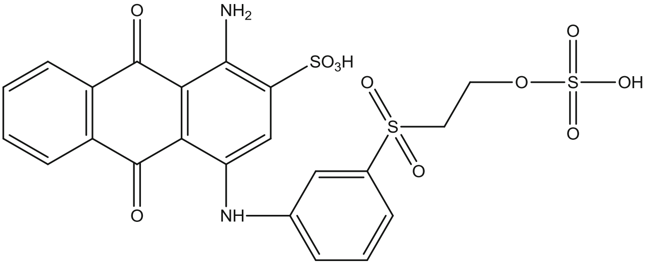


C.I. Reactive Blue 40

Reactive Anthraquinone Dyes

Anthraquinone-based dyes are significant because of their brilliance, chromophore stability under both acidic and basic conditions, and good light-fastness. The shades of anthraquinone dyes are violet to blue. The representative examples of reactive anthraquinone dyes are C.I. Reactive Blue 4 and C.I. Reactive Blue 19 as shown below.


C.I. Reactive Blue 4


C.I. Reactive Blue 19

Solvent Dyes

Solvent dyes are water-insoluble but solvent-soluble dyes, which are generally devoid of polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium salts. These dyes are predominantly azo and anthraquinone but phthalocyanine, triarylmethane, and xanthene are also included. Solubility in an organic solvent or solvents is a characteristic physical property of a solvent dye. Solvent dyes are used for coloring gasoline, inks, oils, plastics, and waxes. A great variety of solvents are employed in the technologies which require the use of solvent dyes and are generally classified based on the solvent as given below:

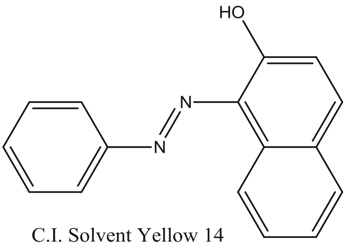
1. Alcoholic solvents (e.g., ethanol, methanol)
2. Ethers, esters, and ketones (e.g., Cellosolve, ethyl acetate, acetone)
3. Aliphatic and aromatic hydrocarbons (e.g., benzene, toluene, xylene, mineral oil, turpentine)
4. Chlorinated hydrocarbons (e.g., carbon tetrachloride, tetrachloroethylene, trichloroethylene)
5. Oils, fats, waxes (e.g., linseed oil, stearic acid, oleic acid, paraffin wax)

It is common practice to use mixed solvents in order to obtain the requisite physical properties and in particular a high power of solvation.

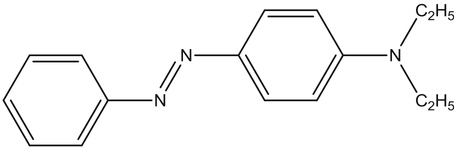
Chemically, solvent dyes are classified as azo and anthraquinone dyes.

Solvent Azo Dyes

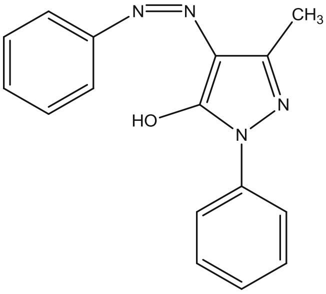
The representative examples of solvent dyes containing azo group are C.I. Solvent Yellow 14, C.I. Solvent Yellow 56, C.I. Solvent Yellow 16, C.I. Solvent Red 23, and C.I. Solvent Red 24 as shown below.



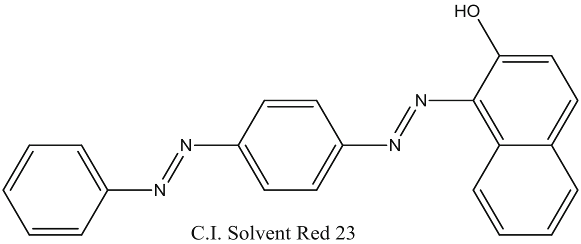
C.I. Solvent Yellow 14



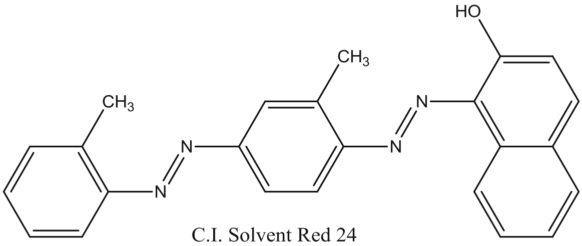
C.I. Solvent Yellow 56



C.I. Solvent Yellow 16



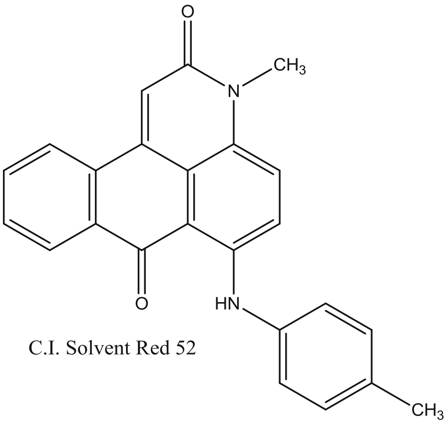
C.I. Solvent Red 23



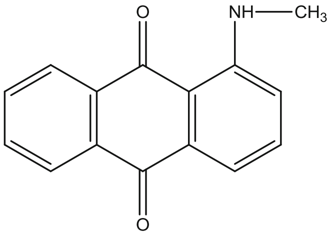
C.I. Solvent Red 24

Solvent Anthraquinone Dyes

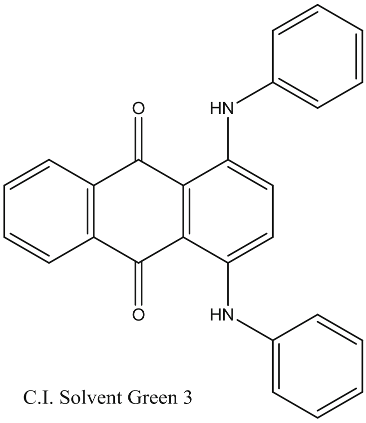
The representative examples of solvent dyes containing anthraquinone nucleus are C.I. Solvent Red 52, C.I. Solvent Red 111, C.I. Solvent Green 3, and C.I. Solvent Violet 13 as shown below.



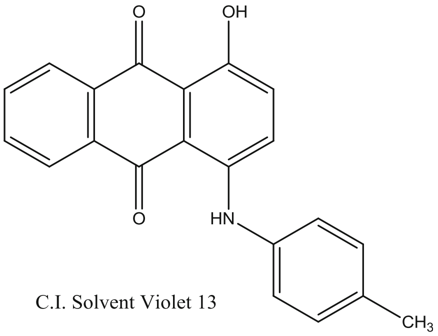
C.I. Solvent Red 52



C.I. Solvent Red 111



C.I. Solvent Green 3



C.I. Solvent Violet 13

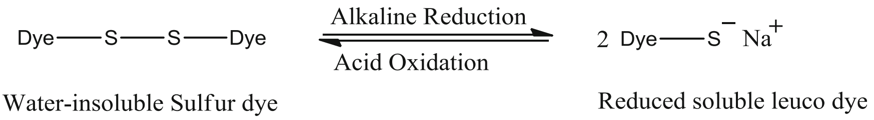
Sulfur Dyes

This is a relatively small group of dyes. The low cost and good wash-fastness properties of the dyeings make this class important from an economic standpoint. However, they are under pressure from an environmental viewpoint. Sulfur dyes are water-insoluble macromolecules, which are characterized by disulfide (S–S) or oligosulfide ($[S–S]_n$) bonds between aromatic residues. Sulfur dyes can be synthesized from aromatic amines, phenols, and aminophenols upon treatment with sulfur or sodium polysulfide or both. In a classical dyeing process, dispersions of sulfur dyes can be reduced with sodium sulfide (Na_2S) at their S–S bonds. The soluble monomeric dye anion is then adsorbed and reoxidized on the fiber [45–47].

Sulfur dyes are divided into three groups:

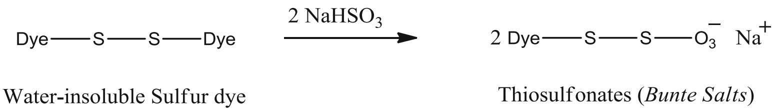
1. **C.I. Sulfur Dyes**
These are classical or conventional sulfur dyes which are water-insoluble, polymeric compounds containing sulfur as integral part of the chromophore. The S–S of the sulfur dye bond must be cleaved (Na_2S, pH $>$ 10) before they become water soluble for dyeing applications. Sulfur dyes in attached polysulfide chains are normally applied in alkaline-soluble reduced form from a sodium sulfide solution and oxidized to their insoluble form in the fiber as shown in Scheme 55.

2. **C.I. Leuco Sulfur Dyes (Pre-reduced)**
These dyes are in “ready-to-use” or “ready-to-dye” form, which are pre-reduced (in reduced form) and contain additional reducing agents for stabilization. The reducing agent most frequently employed is a mixture of sodium sulfide

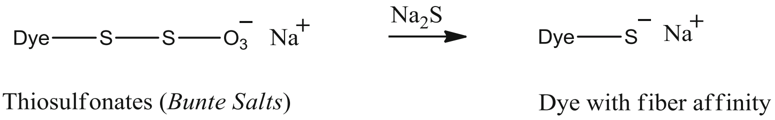


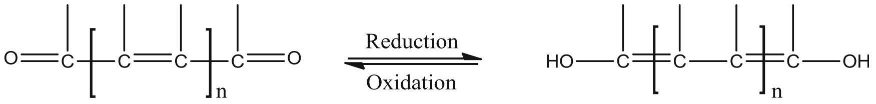
Scheme 55 Reduction and reversible oxidation of sulfur dye

Scheme 56 *Bunte salts*



Scheme 57 Reduction of *Bunte salts*





n = 1 Indigo, benzoquinone, naphthaquinone, anthraquinone

Scheme 58 Vatting

and sodium hydrosulfide to which hydrotropic agents are frequently added.

3. **C.I. Solubilized Sulfur Dyes (Thiosulfonic Acid Derivatives of Sulfur Dyes)**

These dyes are obtained by reacting conventional sulfur dyes (water-insoluble) with sodium sulfite or sodium bisulfite in the presence of atmospheric oxygen to give thiosulfonic acid derivatives, specifically thiosulfonate groups (dye-S-S$^-$Na$^+$) and are called as *Bunte salts* as shown in Scheme 56, which are very soluble in water but possess no affinity for the fiber until reduced in the presence of alkali and reducing agents (Na_2S or NaSH) as shown in Scheme 57 [48]. Sulfur dyes are applied primarily to cotton and rayon. The low cost coupled with their good fastness properties and the ease with which they can be applied to cellulosic fibers continues to ensure high consumption. They also find use in dyeing nylon. Sulfur dyes are used for dyeing paper, particularly used for lamination purposes. Solubilized sulfur dyes (*Bunte salts*) are mainly applied to leather.

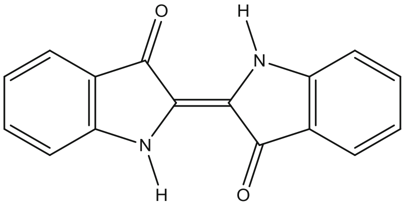
Vat Dyes

Vat dyes are insoluble in water but can be converted or transformed into alkali-soluble form (Leuco form) on treatment with caustic soda and a reducing agent, usually sodium hydrosulfite or hyposulfite ($Na_2S_2O_4$) by reduction. This process of reduction and solubilization is called "vatting" as shown in Scheme 58. The chemical change in vatting is the reduction of quinone or carbonyl groups to alkali-soluble phenolic or enolic groups. The leuco compounds or sodium salts of the reduction products or the "vats" have affinity for textile fibers, especially cotton; and when the impregnated fiber is exposed to air, the leuco compound is reoxidized to the insoluble parent dye. Thus, once applied, air oxidation restores the original color of the dye on the fiber. Typically, vat dyes contain a chain of conjugated double bonds with two keto groups (=C=O) in the end position. The leuco form of the vat dyes with their enol (–OH) groups are only sparingly soluble in water. Hence vat dyes can be easily rendered soluble with sodium dithionite ($Na_2S_2O_4$) in alkaline solution, which is the classical agent for vatting. Vat dyes are regarded as the aristocrats of the cellulosic dyes due to their remarkable stability and outstanding fastness properties; however, the disadvantages of the vat dyes are associated with their high price and the relative difficulty of application. Vat dyes can be applied to wool and also find substantial use for silk [49, 50].

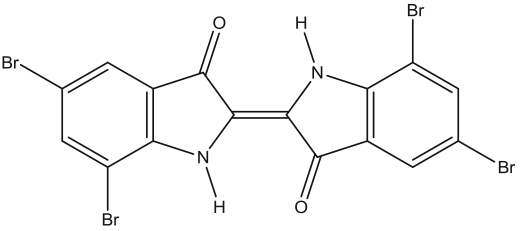
Vat dyes belong to two main chemical classes: (1) indigoid and (2) anthraquinonoid.

Vat Indigoid Dyes

No account of vat dye chemistry would be complete without a mention of indigo (C.I. Vat Blue 1). Indigoid vat dyes are derivatives of indigo and thioindigo. Indigo exits as blue-violet needles or prisms and is practically insoluble in water. It is very stable to heat and light. Indigo is applied as its water-soluble form, produced by reduction with sodium dithionite and a reddish-blue dye, generated on the fabric by oxidation, and extensively used for dyeing of denim. Indigoid vat dyes are mainly used in textile printing. The representative examples of vat indigoid dyes are C.I. Vat Blue 1 and C.I. Vat Blue 5 as shown below.



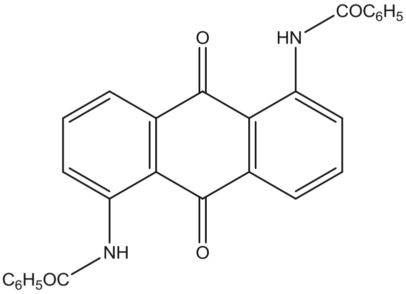
C.I. Vat Blue 1



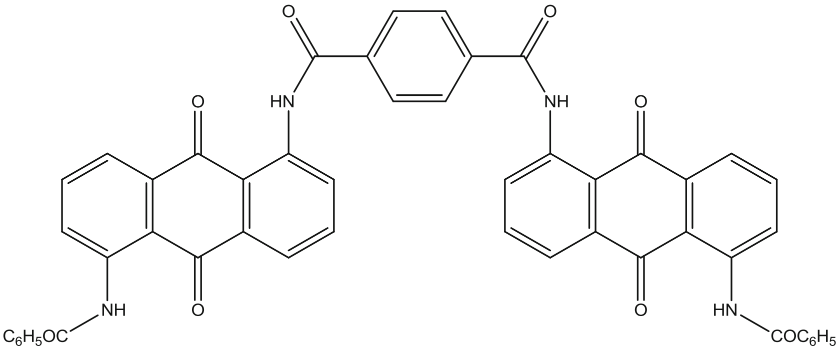
C.I. Vat Blue 5

Vat Anthraquinonoid Dyes

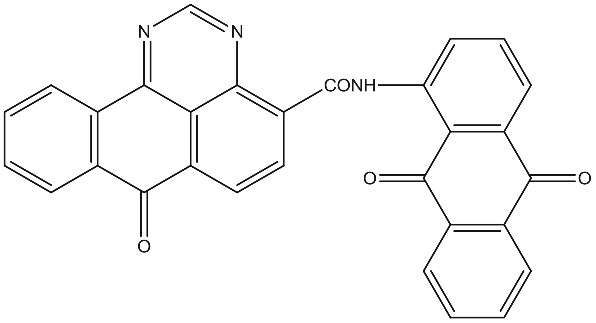
Anthraquinonoid dyes are characterized by their high all-round fastness. The anthraquinonoid vat dyes represent the highest fastness to all agencies so far available among the synthetic dyes and are most valuable dyes for cotton. Acylaminoanthraquinones are mainly used as vat yellows, although it is possible to produce reds and violets. The representative examples of acylaminoanthraquinone vat dyes are C.I. Vat Yellow 3, C.I. Vat Yellow 23, C.I. Vat Yellow 20, and C.I. Vat Red 28 as shown below.



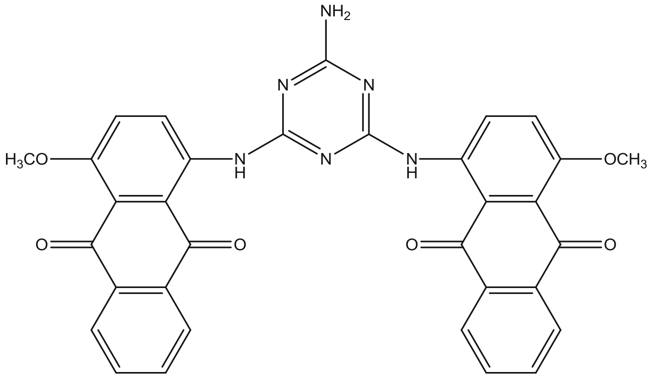
C.I. Vat Yellow 3



C.I. Vat Yellow 23

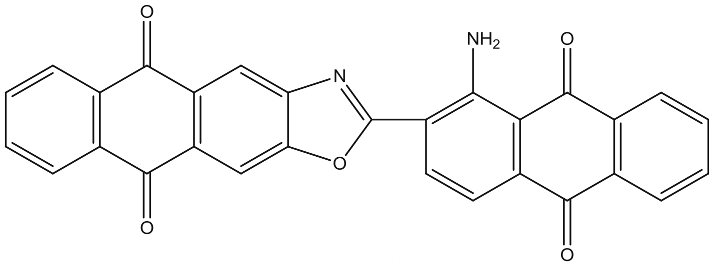


C.I. Vat Yellow 20

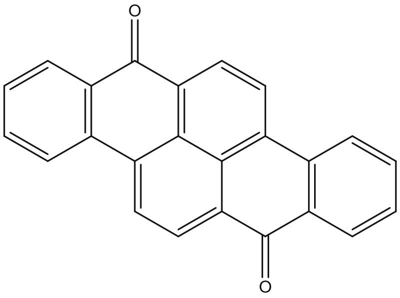


C.I. Vat Red 28

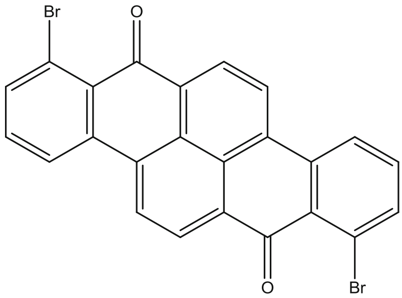
The other representative examples of anthraquinonoid vat dyes are C.I. Vat Red 10, C.I. Vat Yellow 4, C.I. Vat Orange 1, Violanthrone (C.I. Vat Blue 20), and C.I. Vat Green 1 as shown below.



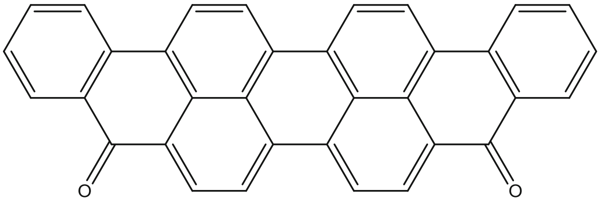
C.I. Vat Red 10



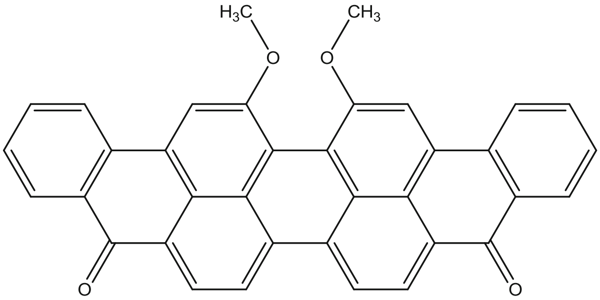
C.I. Vat Yellow 4



C.I. Vat Orange 1



Violanthrone (C.I. Vat Blue 20)



C.I. Vat Green 1

Manufacture of Dyes

In this section, we summarize the principal methods of synthesis for different dye classes. Emphasis is placed on dyes presently in commerce and the industrial methods suitable for making them. Before doing so, we review the important principles that set dyes apart from other classes of organic compounds.

Unlike other organic compounds, dyes possess color because they (1) absorb light in the visible spectrum (400–700 nm), (2) have at least one chromophore (color-bearing group), (3) have a conjugated system (system of

Table 5 Wavelength of light versus color

Wavelength absorbed	Color absorbed	Color observed
400–435	Violet	Yellow–green
435–480	Blue	Yellow
480–490	Green–blue	Orange
490–500	Blue–green	Red
500–560	Green	Purple
560–580	Yellow–green	Violet
580–595	Yellow	Blue
595–605	Orange	Green–blue
605–700	Red	Blue–green

alternating double and single bonds), and (4) exhibit resonance (a stabilizing force in organic compounds). Table 5 shows the relationships between wavelength of visible light and color absorbed/seen.

Acid dyes

The representative examples of the synthetic procedures for the most commercially important acid dyes are described below.

Synthesis of C.I. Acid Yellow 76

4-Aminophenol is diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in alkaline medium with 5-hydroxy-3-methyl-1(4′-sulfophenyl)-pyrazole that gave monoazo dye, followed by esterification with p-tolunene sulfonyl chloride in alkaline medium which yielded C.I. Acid Yellow 76 [51] as shown in Scheme 59. The toluene sulfonic ester group substantially improves the fastness to milling and makes the shade obtained largely independent of pH. The dye is a yellow powder used for dyeing nylon and wool in reddish yellow hues from a neutral bath.

Synthesis of C.I. Acid Blue 129

Condensation of 1-amino-4-bromoanthraquinone-2-sulfonic acid with 1-amino-2,4,6-trimethylbenzene (mesidine) in the presence of sodium bicarbonate and copper powder in ethanol yielded C.I. Acid Blue 129 [52] as shown in Scheme 60. This dye is used for dyeing nylon and wool in bright reddish-blue hues with good light-fastness and wet-fastness.

Synthesis of C.I. Acid Green 25

Condensation of quinizarin (1,4-dihydroxyanthraquinone) with excess of p-toluidine in the presence of hydrochloric acid, boric acid, and zinc dust, followed by sulfonation with oleum, gave C.I. Acid Green 25 [51] as shown in Scheme 61. This dye is a dark greenish powder, used for dyeing nylon and wool in green hues with good light-fastness and wet-fastness.

Basic Dyes

The representative examples of the synthetic procedures for the most commercially important basic dyes are described below.

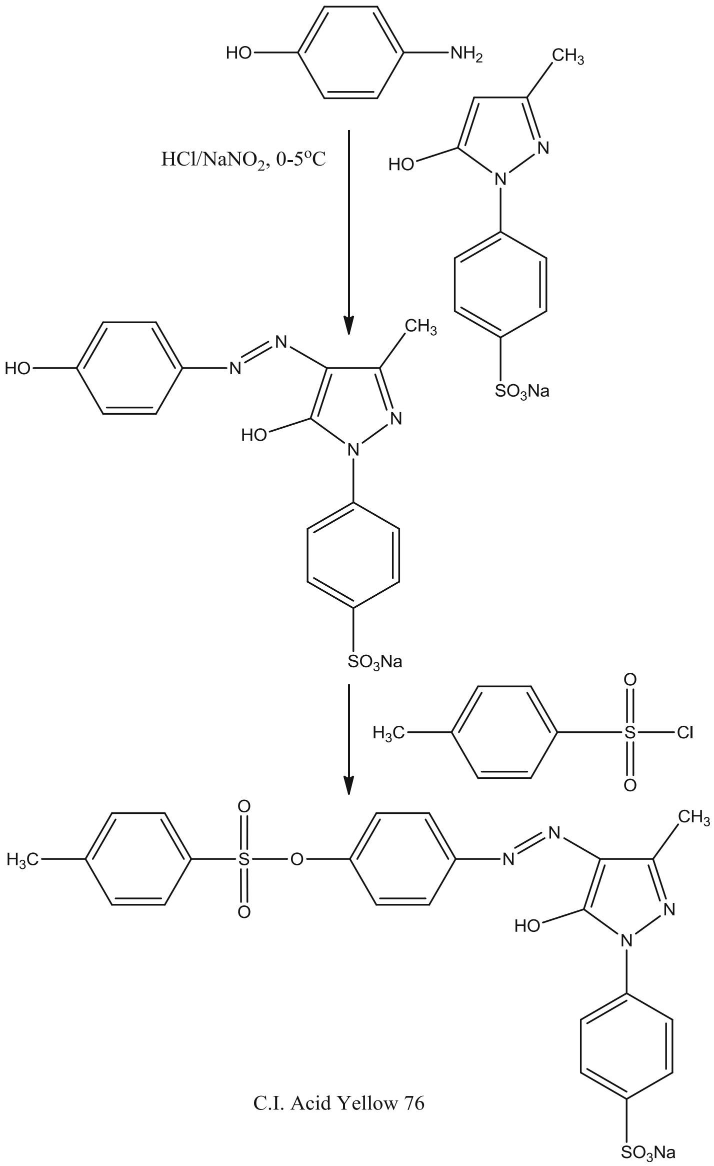
Synthesis of C.I. Basic Yellow 11

Fischer’s aldehyde is condensed with 2,4-dimethoxyaniline in the presence of alcohol which gave C.I. Basic Yellow 11 [53, 54] as shown in Scheme 62. It provides bright greenish-yellow shade having good light-fastness.

Synthesis of C.I. Basic Red 14

Fischer’s base is condensed with 4-formyl-N-methyl-N-2-cyanoethylaniline in acid which gave C.I. Basic Red 14 [55] as shown in Scheme 63. It is a bright, fluorescent, cationic red hemicyanine dye with high tinctorial strength but moderate light-fastness.

Scheme 59 Synthesis of C.I. Acid Yellow 76

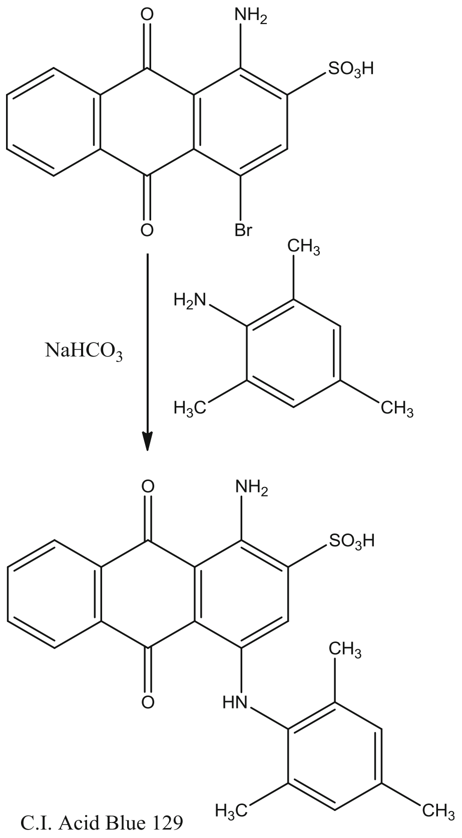


Synthesis of C.I. Basic Blue 3

N,N-Diethyl-3-anisidine is nitrosated with hydrochloric acid and sodium nitrite to corresponding 4-nitroso derivative, which is condensed with N,N-diethyl-3-aminophenol in ethanol, that resulted in C.I. Basic Blue 3 as shown in Scheme 64 [56]. It is a bright dye with good light-fastness property.

Synthesis of C.I. Basic Blue 22

1-Methylaminoanthraquinone upon bromination gave 4-bromo-1-methylaminoanthraquinone, which is treated with 1-amino-3-N,N-dimethylaminopropane, followed by quaternization with dimethyl sulfate which gave C.I. Basic Blue 22 [57] as shown in Scheme 65. It demonstrates high fastness to heat treatment and to the dye bath hydrolysis.



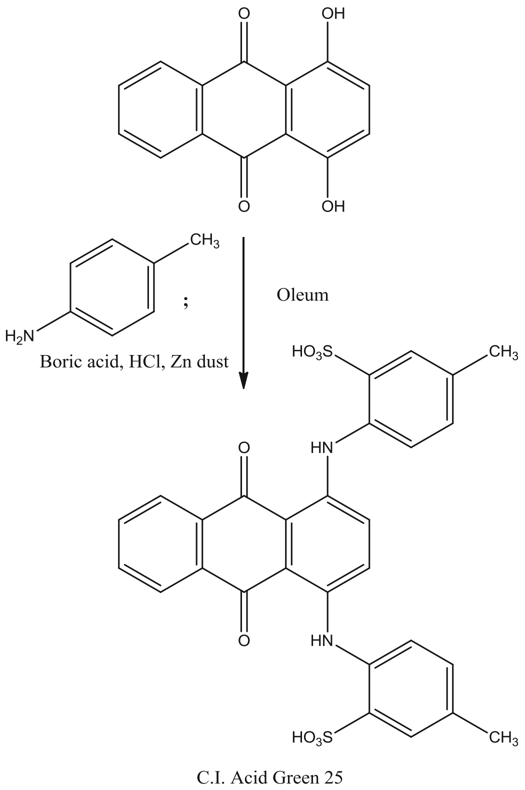
Scheme 60 Synthesis of C.I. Acid Blue 129

Direct Dyes

The representative examples of the synthetic procedures for the most commercially important direct dyes are described below.

Synthesis of C.I. Direct Red 16

Aniline is diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in alkaline medium with J-acid which gave monoazo dye. The monoazo dye is further diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in alkaline medium with J-acid which gave C.I. Direct Red 16 [58] as shown in Scheme 66.



Scheme 61 Synthesis of C.I. Acid Green 25

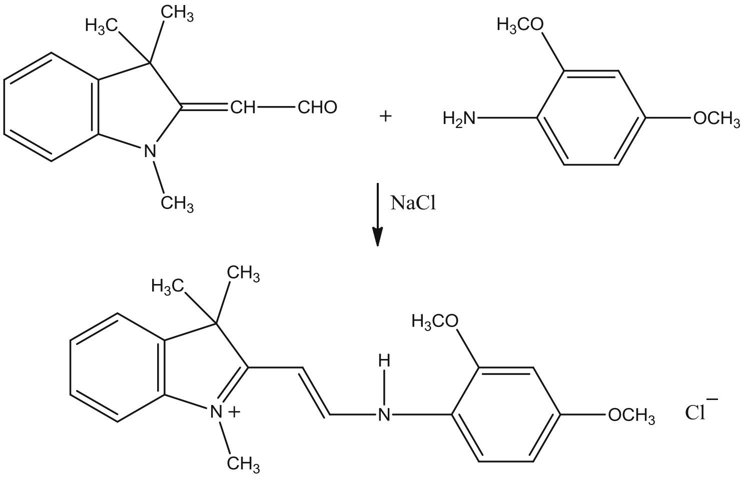
Synthesis of C.I. Direct Blue 67

H-acid is diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in acidic medium with 2-methoxy-5-methylaniline which gave monoazo dye. The monoazo dye is further diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in alkaline medium with phenyl-J-acid which gave C.I. Direct Blue 67 [58] as shown in Scheme 67. It is a bright blue dye with good fastness properties.

Synthesis of C.I. Direct Green 13

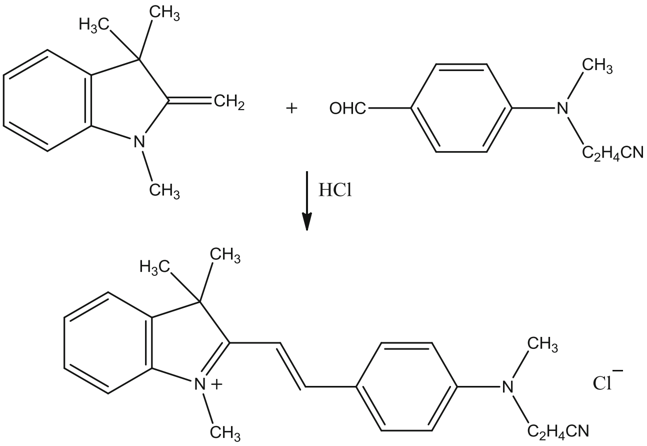
4-Aminobiphenyl-3-sulfonic acid is diazotized in concentrated hydrochloric acid and sodium

Scheme 62 Synthesis of C.I. Basic Yellow 11

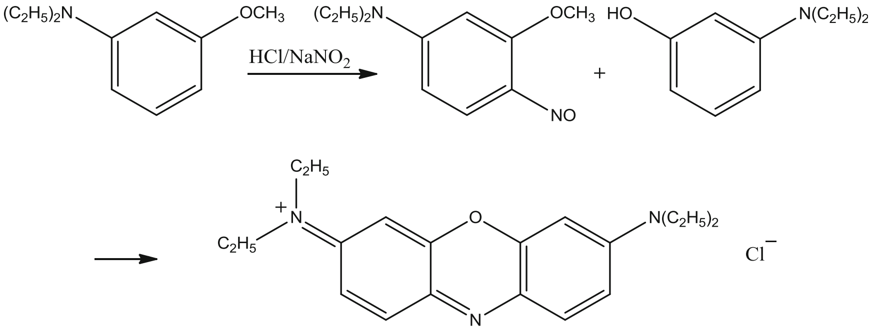


C.I. Basic Yellow 11

Scheme 63 Synthesis of C.I. Basic Red 14

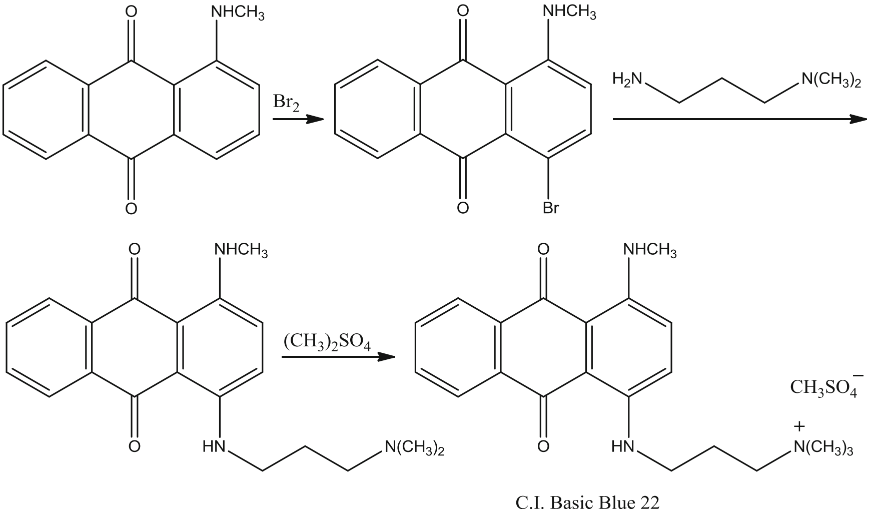


C.I. Basic Red 14



C.I. Basic Blue 3

Scheme 64 Synthesis of C.I. Basic Blue 3



Scheme 65 Synthesis of C.I. Basic Blue 22

nitrite at 0–5 °C and coupled in acidic medium with 1-amino-2-ethoxynaphthalene-6-sulfonic acid which gave monoazo dye. The monoazo dye is further diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in alkaline medium with benzoyl-H-acid which gave C.I. Direct Green 13 [58] as shown in Scheme 68.

Disperse Dyes

The representative examples of the synthetic procedures for the most commercially important disperse dyes are described below.

Synthesis of C.I. Disperse Blue 284 and C.I. Disperse Green 9

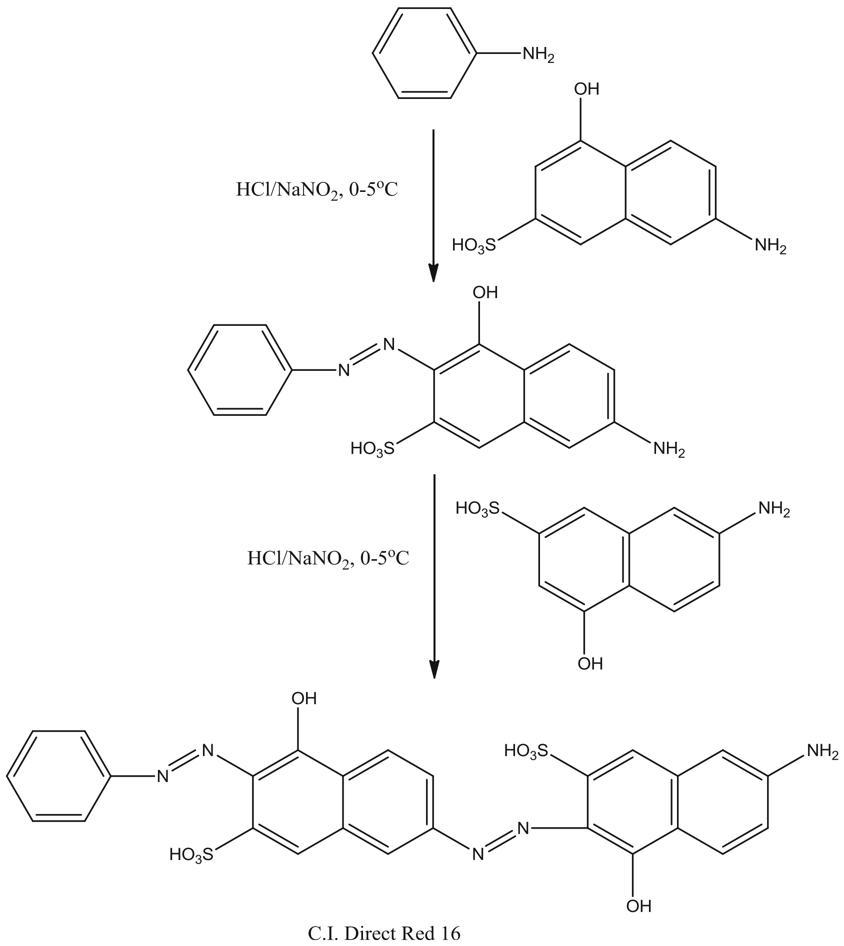
The most facile and promising set of synthetic routes for the preparation of 2-aminothiophenes with both a high and varied degree of substitution was discovered by Karl Gewald [32, 59–62]. This discovery spurred much research efforts, as evidenced by the profusion of patent literature. ICI chemists commercialized dyes based on Gewald reaction which are C.I. Disperse Blue 284 and C.I. Disperse Green 9 [32]. The key intermediate, 2-amino-3,5-dinitrothiophene, was synthesized by Gewald reaction. 2-Amino-3,5-dinitrothiophene is diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in acidic medium with corresponding N, N-dialkylsubstituted aryl amine that gave C.I. Disperse Blue 284 and C.I. Disperse Green 9, respectively, are as shown in Scheme 69 and in Scheme 70.

Synthesis of C.I. Disperse Yellow 33

4-Chloro-3-nitrobenzenesulfonamide is condensed with aniline in the presence of sodium carbonate that gave C.I. Disperse Yellow 33 [63] as shown in Scheme 71.

Synthesis of C.I. Disperse Yellow 42

4-Chloro-3-nitrobenzenesulfonyl chloride is condensed with two equivalents of aniline in the presence of sodium carbonate that gave C.I. Disperse Yellow 42 [64] as shown in Scheme 72.



Scheme 66 Synthesis of C.I. Direct Red 16

Synthesis of C.I. Disperse Blue 60

Condensation of 1,4-diaminoanthraquinone-2,3-dicarboximide with *gamma*-methoxypropylamine in nitrobenzene yielded C.I. Disperse Blue 60 as shown in Scheme 73. The dye is used for dyeing polyethylene terephthalate and cellulose acetate fibers in bright blue shade exhibiting good light-fastness and wash-fastness [65].

Reactive Dyes

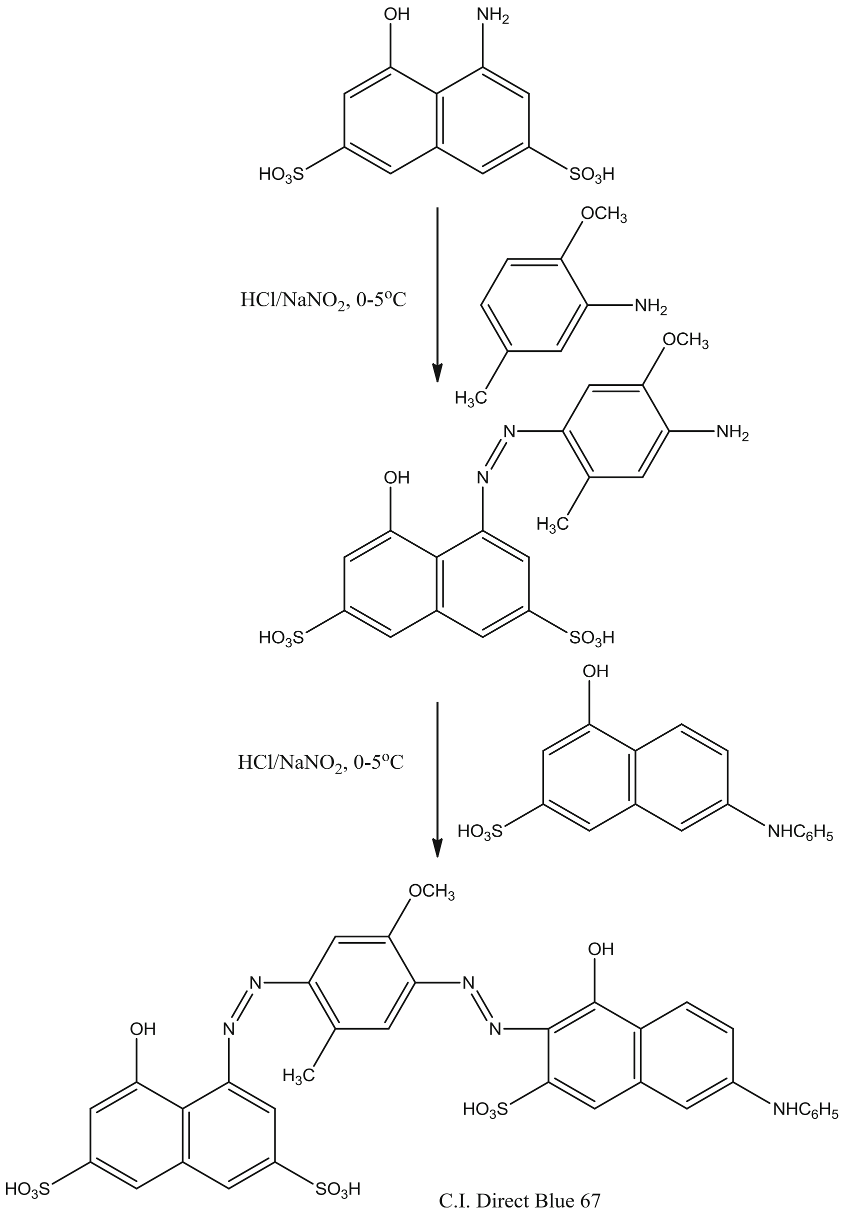
The representative examples of the synthetic procedures for the most commercially important reactive dyes are described below.

Synthesis of C.I. Reactive Yellow 4

2-Aminonaphthalene-4,8-disulfonic acid is diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in acidic medium with m-toluidine that gave monoazo dye. Condensation of monoazo dye with cyanuric chloride yielded C.I. Reactive Yellow 4 [66] as shown in Scheme 74.

Synthesis of C.I. Reactive Orange 1

Aniline-2-sulfonic acid is diazotized in concentrated hydrochloric acid and sodium nitrite at 0–5 °C and coupled in alkaline medium

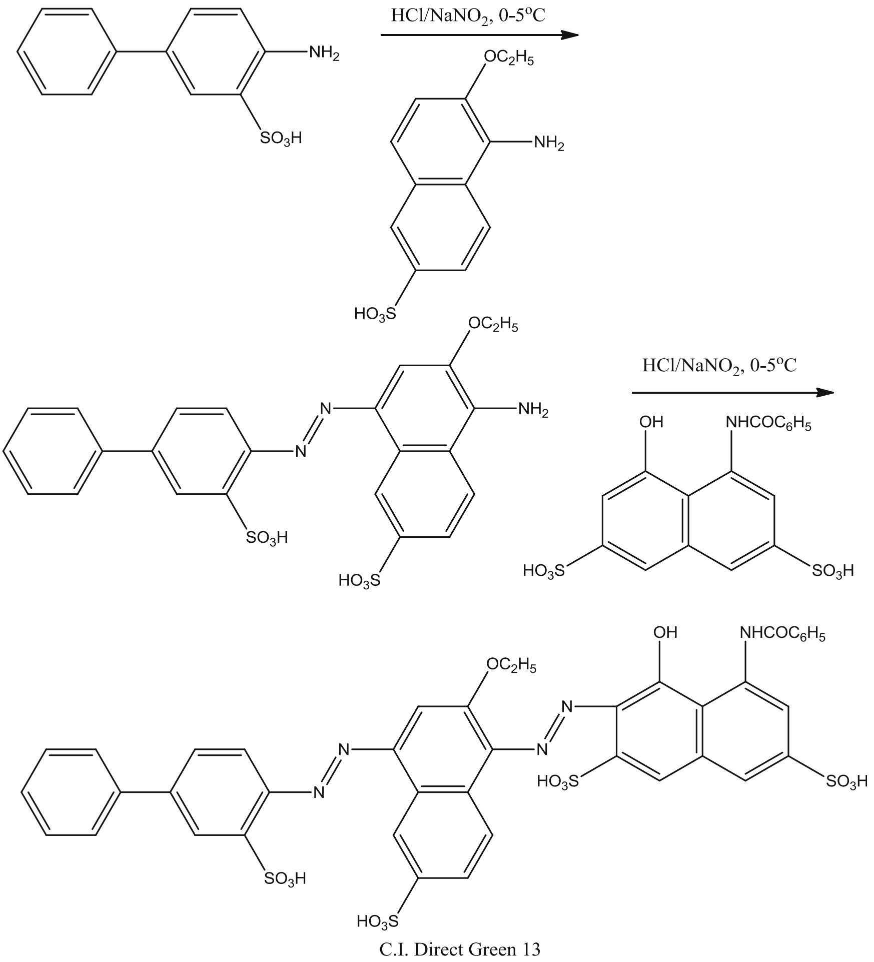


Scheme 67 Synthesis of C.I. Direct Blue 67

with J-acid that gave monoazo dye. Condensation of monoazo dye with cyanuric chloride yielded C.I. Reactive Orange 1 [67] as shown in Scheme 75. It is also possible to condense the reactive system with the coupler prior to reaction with the diazonium component.

Vat Dyes

The representative examples of the synthetic procedures for the most commercially important vat dyes are described below.



Scheme 68 Synthesis of C.I. Direct Green 13

Synthesis of Indigo (C.I. Vat Blue 1)

Indigo (C.I. Vat Blue 1) was first synthesized by A von Baeyer from phenylacetic acid with a series of reactions to isatin, which is converted to indigo by treating with phosphorus trichloride and phosphorus in acetyl chloride [68, 69] as given in Scheme 76.

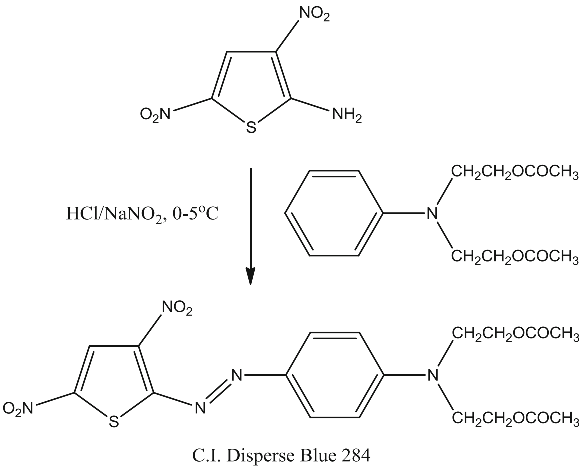
Synthesis of Indigo (C.I. Vat Blue 1)

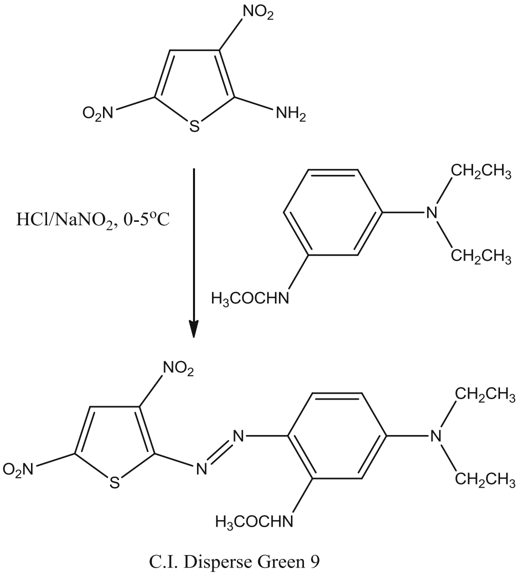
Indigo was prepared by Karl Heumann by reacting aniline with chloroacetic acid to form N-phenylglycine salt followed by fusing the salt with potassium hydroxide to convert it to indoxylate salt which is finally hydrolyzed and oxidized to form indigo [70] as given in Scheme 77.

Synthesis of C.I. Vat Yellow 4 and C.I. Vat Orange 1

Naphthalene is reacted with benzoyl chloride in the presence of aluminum chloride that gave 1,5-dibenzoylnaphthalene, which on treatment with aluminum chloride and sodium chloride in the presence of air gave dye C.I. Vat Yellow 4 as shown in Scheme 78, followed by dropwise addition of bromine yielding another dye, C.I. Vat Orange 1 as shown in Scheme 78 [71].

Scheme 69 Synthesis of C.I. Disperse Blue 284





Scheme 70 Synthesis of C.I. Disperse Green 9

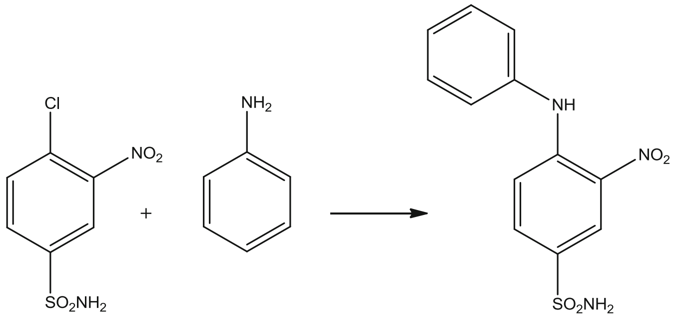
Synthesis of Violanthrone (C.I. Vat Blue 20) and C.I. Vat Green 1

Benzanthrone serves as a starting material for the synthesis of Violanthrone (C.I. Vat Blue 20) and C.I. Vat Green 1. Benzanthrone is stirred and heated in isobutyl alcohol, potassium hydroxide, and sodium acetate under basic condition followed by oxidation with sodium hypochlorite that gave 4,4′-dibenzanthronyl, which serves as a key intermediate for the preparation of Violanthrone (C.I. Vat Blue 20) and C.I. Vat Green 1. 4,4′-Dibenzanthronyl is reacted with potassium hydroxide and potassium acetate, under stronger alkaline condition, followed by oxidation, that cyclizes to Violanthrone (C.I. Vat Blue 20) as shown in Scheme 79. Similarly, benzanthrone is converted to 4,4-′-dibenzanthronyl, which under acidic oxidative conditions (H_2SO_4/MnO_2) followed by treatment with sodium bisulfite ($NaHSO_3$) gave 16,17-dihydroxyviolanthrone. Upon treatment with sodium carbonate and dimethyl sulfate, 16,17-dihydroxyviolanthrone gave 16,17-dimethoxyviolanthrone (C.I. Vat Green 1) [72] as shown in Scheme 80.

Production and Sales

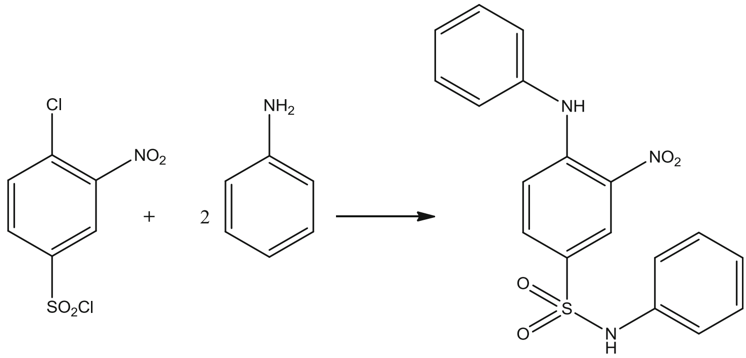
During the 1990s, the large international companies began to form alliances with producers around the world. Hoechst AG, which had done little research on disperse dyes since the 1970s, signed an agreement in 1990 with Mitsubishi of Japan and gained access to a strong line of disperse dyes. BASF AG and Mitsui signed agreements for vat dyes. ATIC resulted from a joint venture between ICI and

Scheme 71 Synthesis of C.I. Disperse Yellow 33

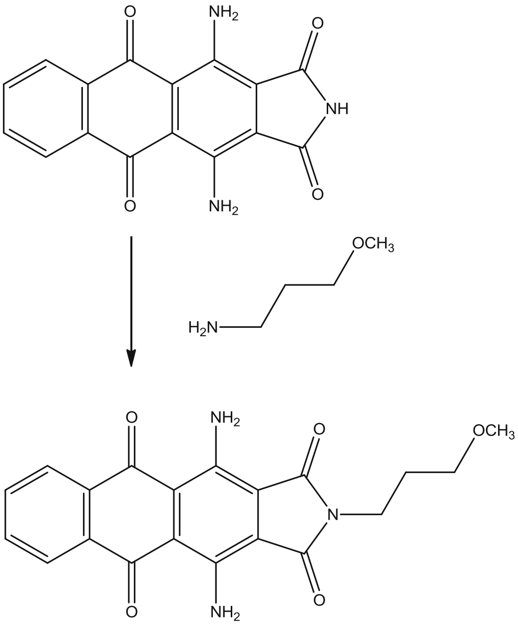


C.I. Disperse Yellow 33

Scheme 72 Synthesis of C.I. Disperse Yellow 42



C.I. Disperse Yellow 42

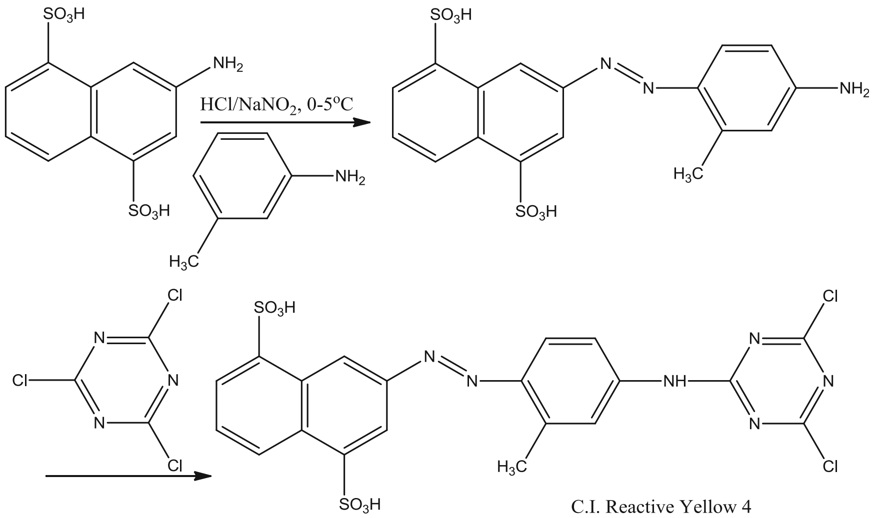


C.I. Disperse Blue 60

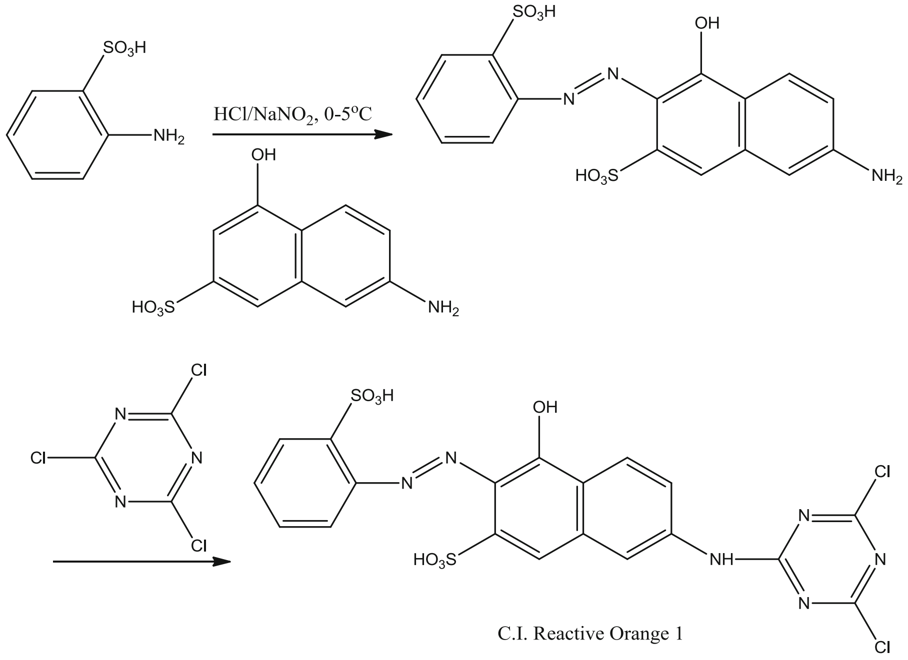
Scheme 73 Synthesis of C.I. Disperse Blue 60

Atul of India. Finally, a major break came in January 1995, when Bayer AG and Hoechst AG, the parent companies in Germany, announced the formation of DyStar, a worldwide consolidation of their textile dye businesses, which included the US Hoechst Celanese, and Bayer. Within a short time, BASF acquired the textile dye business of ICI/Zeneca. Swiss companies Ciba and Clariant (derived by consolidating Sandoz and portions of Hoechst in 1995) announced a merger of the textile dye business but cancelled the venture in 1998. Crompton & Knowles (C&K) emerged as the sole US-based major company, but the company struggled during the late 1990s and was sold to Yorkshire Group PLC of the United Kingdom. Yorkshire Pat-Chem and C&K became Yorkshire Americas.

Globalization and establishment of NAFTA meant fewer textile dyes were needed and manufactured in the United States during the

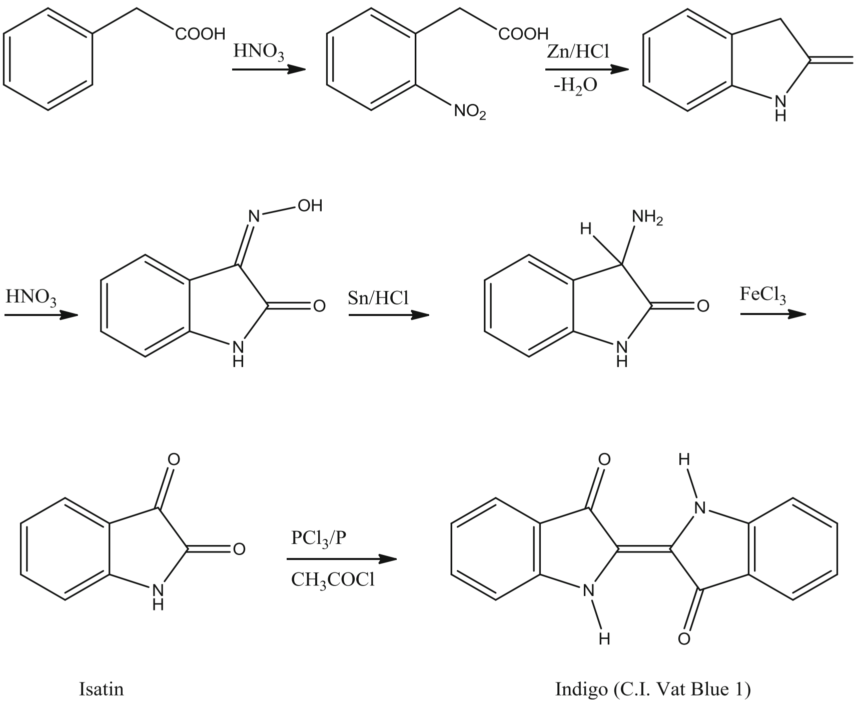


Scheme 74 Synthesis of C.I. Reactive Yellow 4



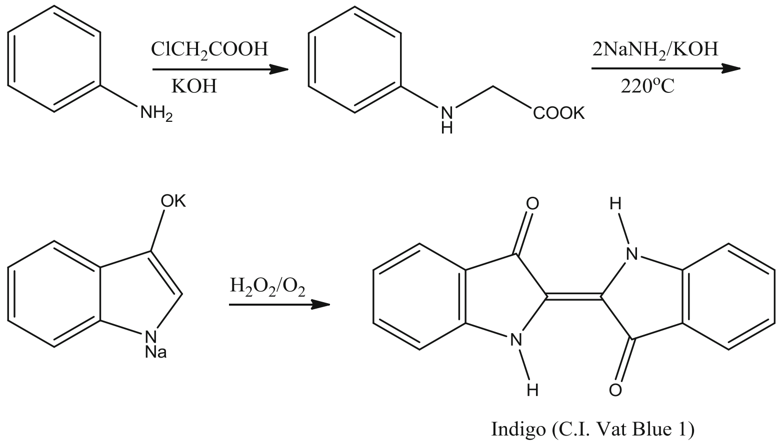
Scheme 75 Synthesis of C.I. Reactive Orange 1

late 1990s. The market shrank from 232 million pounds ($955 million) in 1994 to 214 million pounds ($689 million) in 1998 with further cuts were expected. Imported dyes expanded but prices fell. Some 1.1 million pounds of disperse dyes were brought in with a value of $5 million in 1992. In 1999, 5.7 million pounds with a value of $10 million were imported. For each class of dyes, you can find expansion of imports for fewer and fewer dollars. The latest year when consumption was publicly revealed is given in Table 6.



Scheme 76 Synthesis of Indigo (C.I. Vat Blue 1)

Scheme 77 Synthesis of Indigo (C.I. Vat Blue 1)

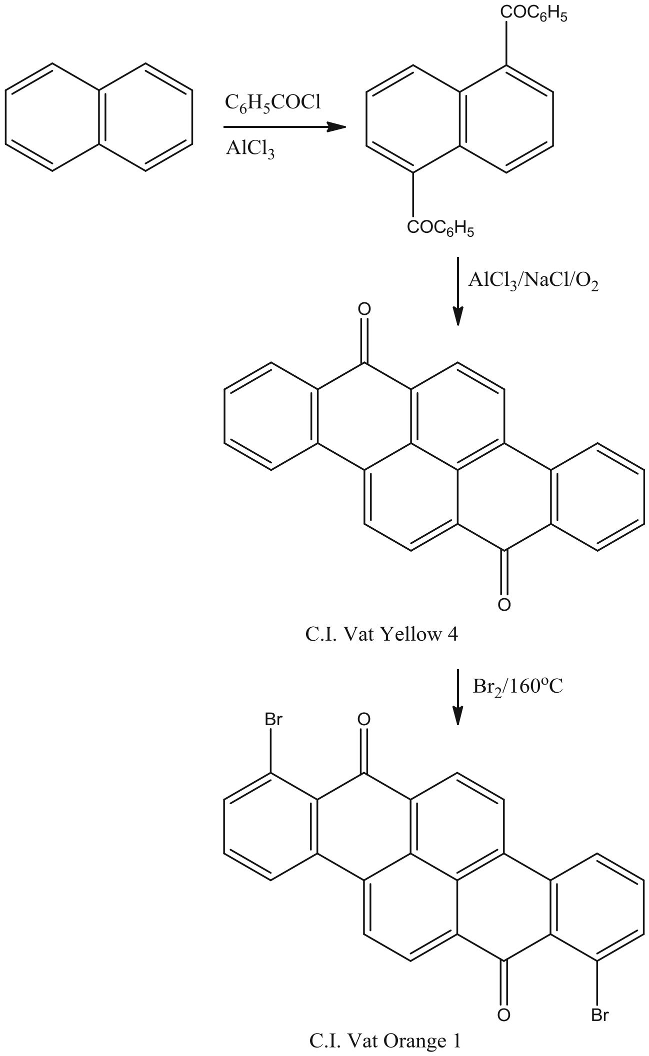


Industrial Applications of Dyes

Textile Applications of Dyes

The process of dyeing may be carried out in batches or on a continuous basis. The fiber may be dyed as stock, yarn, or fabric. However, no matter how the dyeing is done, the process is always fundamentally the same: dye must be transferred from a bath—usually aqueous—to the fiber itself. The basic operations of dyeing include (1) preparation of the fiber, (2) preparation of the dye bath, (3) application of the dye, and (4) finishing. There are many variations of

Scheme 78 Synthesis of C.I. Vat Yellow 4, and C.I. Vat Orange 1



these operations, depending on the kind of dye. The dyeing process is complicated by the fact that single dyes are seldom used. The matching of a specified shade may require from two to a dozen dyes.

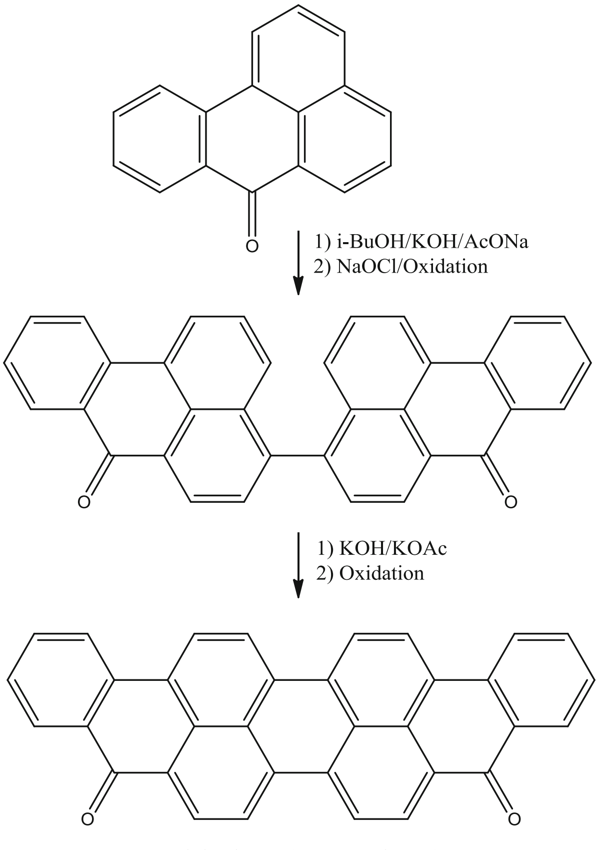
Fiber Preparation

Fiber preparation ordinarily involves scouring to remove foreign materials and ensure even access to dye liquor. Some natural fibers are contaminated with fatty materials and dirt, and synthetic fibers may have been treated with spinning lubricants or sizing that must be removed. Some fibers also may require bleaching before they are ready for use.

Dye Bath Preparation

Preparation of the dye bath may involve simply dissolving the dye in water, or it may be necessary to carry out more involved operations such as reducing the vat dyes. Wetting agents, salts, "carriers," retarders, and other dyeing

Scheme 79 Synthesis of Violanthrone (C.I. Vat Blue 20)



Violanthrone (C.I. Vat Blue 20)

assistants may also be added. Carriers are swelling agents that improve the dyeing rate of very hydrophobic fibers such as the polyesters. Examples are *o*-phenylphenol and biphenyl. Retarders are colorless substances that compete with dyes for dye sites or form a complex with the dye in the bath and act to slow the dyeing rate. Their use is necessary when too rapid dyeing tends to cause unevenness in the dyeings.

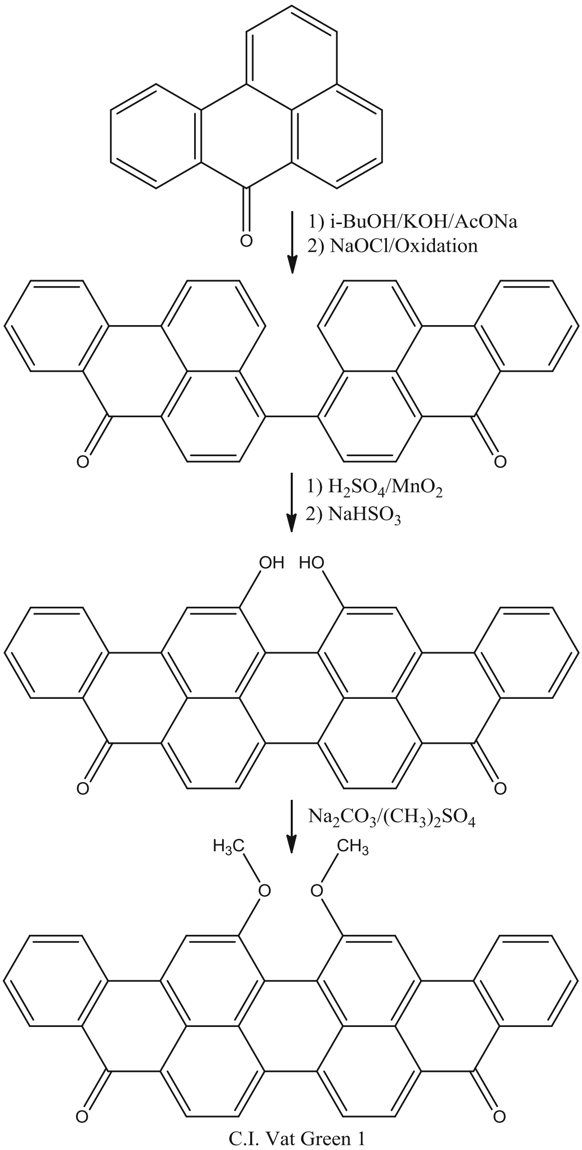
Finishing

The finishing steps for many dyes, such as the direct dyes, are very simple: the dyed material merely is rinsed and dried. Vat-dyed materials, on the other hand, must be rinsed to remove the reducing agent, oxidized, rinsed again, and soaped before the final rinsing and drying steps are carried out. Generally, the finishing steps must fix the color (if fixation has not occurred during application) and remove any loose dye from the surface of the colored substrate. Residual dyeing assistants such as carriers must also be removed.

The types of textile structures that lend themselves to continuous dyeing methods are woven and tufted carpets. Continuous dyeing is designed for long runs of similar product; it is a high-output method of dye application.

The first volume-yardage continuous process was the continuous pad-steam process for vat

Scheme 80 Synthesis of C.I. Vat Green 1



dyes on cotton. The vat dye dispersion was padded onto the cloth and dried; this was followed by passage through a reducing bath, steaming for 30 s, passage through an oxidizing bath, and, finally, washing. When it was discovered that disperse dyes could be thermosoled into polyesters by treatment with dry heat for 60 s and 400 °F, this procedure was readily adapted to continuous processing. The advent of large volumes of dyed polyester-cotton-blend fabrics in the late 1960s made it possible to combine these two processes into one thermosol pad-steam system.

Tufted nylon carpet grew to be the number-one floor covering in the United States in recent decades. Continuous open-width ranges were developed but not without a great deal of ingenuity to deliver the precise loading of liquid to the tufted surface. This was accomplished by a dye applicator that flooded the dye solution onto the carpet surface. The advancing technology in continuous, metered dyeing systems has created a need for dyes in liquid form, both dispersions and solution. The dyes used in carpet dyeing, for the most part, are supplied by the dye manufacturers as liquids (Fig. 3).

Dyeing Methods/Batch

Virtually all types of textile structures are dyed by batch (or exhaust) methods of dyeing, such as stock, yarn, circular knits, warp knits, woven fabrics, garments, and carpets. Batch methods include beck dyeing, jig dyeing, pad-batch, beam dyeing, and others. These methods are dictated primarily by the physical structure of the textile product and the type of fiber(s) it contains. Each of these batch methods employs a different type of machine. As an example, a circular knit fabric comprised of cotton could be dyed in a beck, whereas the same structure comprised of polyester most likely would be dyed in a high-pressure jet machine, and a garment constructed from the circular knit cotton likely would be dyed in a garment machine.

Table 6 World market textile dyes 2002 volume[a]

	Volume tons	%
Reactive	179,381	28
Direct	15,986	3
Vats	18,663	3
Indigo	35,159	6
Sulfur	92,873	15
Disperse	175,845	28
Acid	23,257	4
Metal complex	17,202	3
Chrome	5519	1
Cationic	18,568	3
Naphthol	8942	1
Phthalogen	591	0
Pigment prep.	46,885	7
Total	**638,871**	**100**

[a]Market Survey DyStar 2002

Stock dyeing often is carried out in large heated kettles made of stainless steel or other corrosion-resistant metal. These kettles can be sealed and used for dyeing at temperatures somewhat above the boiling point of water at atmospheric pressure.

Yarns are dyed in package machines. In this arrangement the yarn is wound onto perforated dye tubes and placed on spindles that are fit into a closed kettle. The dye solution is heated and pumped through the spindle and yarn package. A cycle of inside-outside flow usually is used to provide level dyeing by equal exposure of the dye to yarns. Although the basis of package dyeing has not changed, a number of refinements have been introduced in recent years. Precision winding of the yarn has improved quality by giving a more uniform package density. Horizontal machines and valving between chambers to allow reconfiguration of the dye machine to control the size of the dyeing have changed the way package dye houses are built. Robotization has been widely utilized to load and unload

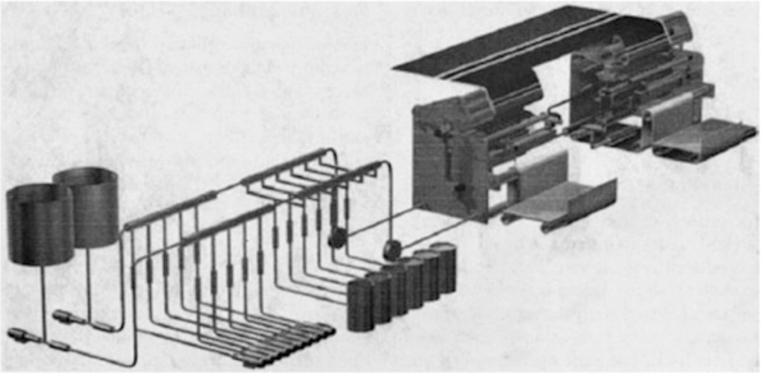


Fig. 3 Fluidyer carpet range dye applicator (Courtesy of Zima Corporation)

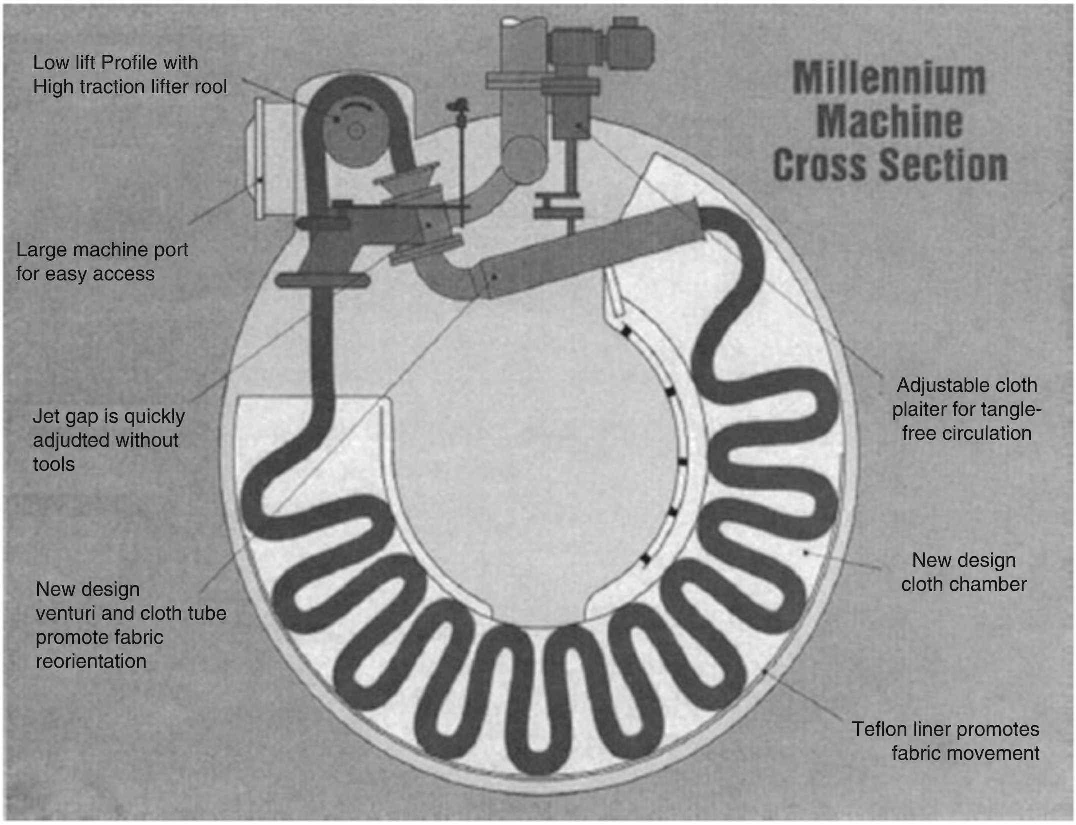


Fig. 4 Millennium jet dyeing machine (courtesy of Gaston County Dyeing Machine Co.)

machines. Also lower ratio dye baths with higher flow rates have improved the energy efficiency of the newer machines.

Fabrics are dyed in machines that move them through the dye liquor either under tension (jig) or relaxed (beck). Fabrics can also be dyed in full width by winding them on a perforated beam through which hot dye liquor is pumped. This is the principle of the beam dyeing machine.

The pressure-jet dyeing machine is unique in that it has no moving parts. The cloth, in rope form, is introduced into a unidirectional liquid stream enclosed in a pipe. Liquor is pumped through a specially designed venturi jet imparting a driving force that moves the fabric. The two fabric ends are sewn together to form a continuous loop.

The first jet machine was introduced in 1965. There are two major types of jet dyeing machines: the vertical kier and the elongated horizontal kier (Fig. 4). In general, the kier uses small water volumes, whereas the elongated types use larger volume ratios in dyeing. The kier types normally are used for more substantial fabrics, and the elongated types are suited for fine or delicate fabric styles. Important features in today's machines are improved corrosion-resistant alloys and the ability to operate at higher efficiencies with minimum energy consumption. The control systems have been refined; there is simultaneous loading and unloading. Larger capacity machines are also being built; a jet dye machine has been developed for carpet dyeing.

Printing

Printing is a special kind of localized dyeing that produces patterns. Four kinds of printing have long been recognized: (1) direct, (2) dyed, (3) discharge, and (4) resist. In direct printing, a thickened paste of the dye is printed on the fabric to produce a pattern. The fabric then is steamed to fix the dye and is finished by washing and drying. Dyed printing requires that the pattern be printed on the fabric with a mordant. The entire piece then is placed in a dye bath containing a mordant dye, but only the mordanted areas are dyeable. Washing then clears the dye from the unmordanted areas, leaving the pattern in color.

In discharge printing, the cloth is dyed all over and then printed with a substance that can destroy the dye by oxidation or reduction, leaving the pattern in white. When a reducing agent such as sodium hydrosulfite is used to destroy the dye, the paste may contain a reduced vat dye. Finishing the goods by oxidation and soaping then produces the pattern in color. In resist printing, certain colorless substances are printed on the fabric. The whole piece then is dyed, but the dye is repelled from the printed areas, thus producing a colored ground with the pattern in white.

Printing is most often done with rotary screens etched in the design to be printed. Printing paste is fed constantly to the center of the rotating screen from a nearby supply, and a squeegee pushes the colored paste through the holes in the screen, leaving the dye paste only in the intended areas; a separate screen is required for each color in the pattern (Fig. 5).

An important recent advance in the pattern coloring of textiles is ink-jet or digital printing. Milliken's Millitron and Zimmer's ChromoJet have been successfully used for carpet and upholstery markets for over two decades. Finer resolution machines began to emerge in the late 1980s when Stork introduced a prototype machine. During the past 5 years a number of manufacturers have introduced digital ink-jet printers that use either CYMK (cyan, yellow, magenta, and black) to make a composite color or true-color machines that use mixed pigment systems. The current machines are very successful at furnishing one of a kind and for use in rapid prototyping.

Pigment Dyeing and Printing

Pigment dyeing and printing are processes that compete with the more conventional means of dyeing and printing described above. These processes use water-insoluble dyes or pigments that are bound to the surfaces of fabrics with resins. A paste or an emulsion, containing pigment and resin or a resin former, is applied to the fabric. The goods then are dried and cured by heat to produce the finished dyeing or print. During the heating or curing, fabric, resin, and pigment become firmly bonded together. This method of color application is economical and produces good results. It should be noted that the pigment is confined to the surface of the fabric and can be selected without regard for fiber affinity.

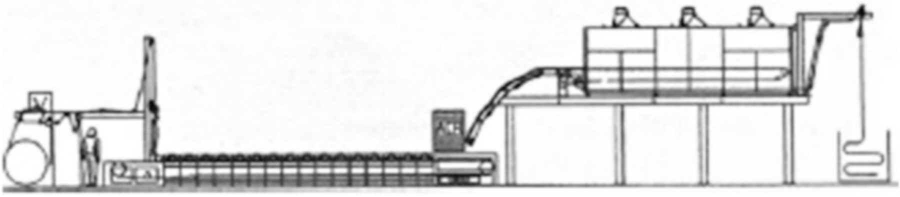


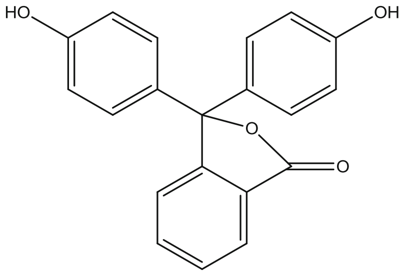
Fig. 5 Rotascreen V rotary screen print machine (courtesy of Zimmer Machinery Co.)

Non-textile Applications of Dyes

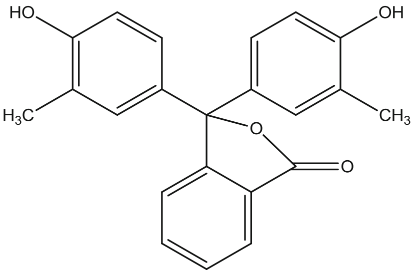
Non-textile applications of dyes include dyes as acid-base indicators (pH indicators), liquid crystal dyes, color filter dyes for displays and sensors, ink-jet dyes, infrared absorbing dyes, laser dyes, photographic dyes, hair dyes, food dyes, and biomedical dyes as discussed below.

Dyes as Acid-Base Indicators (pH Indicators)

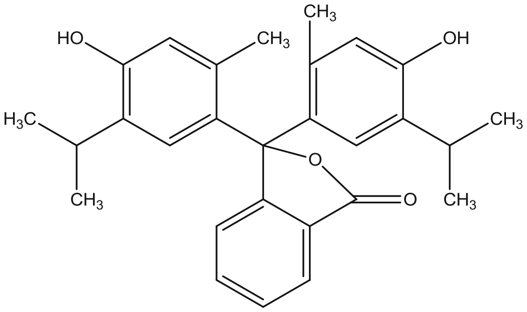
Baeyer's work on phenolphthalein was a major breakthrough in acid-base indicator chemistry in the early days. Baeyer's invention on phthalein dyes has not only revolutionized color chemistry, in general, but also has made a major breakthrough, particularly for the color-change concept with dyes [73–75]. Acid-base indicators are also known as pH indicators. Acid-base indicators are dyes which change color with a change in pH. They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions. The acid-base indicators are grouped into following classes: (1) azo, (2) benzein, (3) nitro, (4) phthalein, (5) sulfonephthalein, (6) triphenylmethane, (7) fluorescent, and (8) miscellaneous and all the pH indicators are summarized systematically in a book [76]. Phthalein dyes/indicators constitute a major class and are most widely used. The representative examples of commonly used phthalein dyes/indicators are phenolphthalein, o-cresolphthalein, and thymolphthalein as shown below.



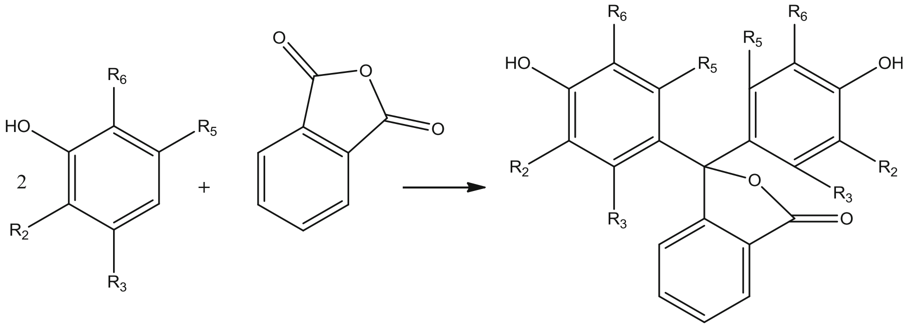
Phenolphthalein



o-Cresolphthalein



Thymolphthalein



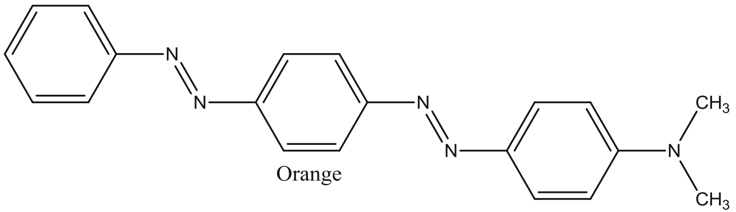
Scheme 81 Synthesis of phthalein dyes/indicators

Synthesis of Phthalein Dyes/Indicators

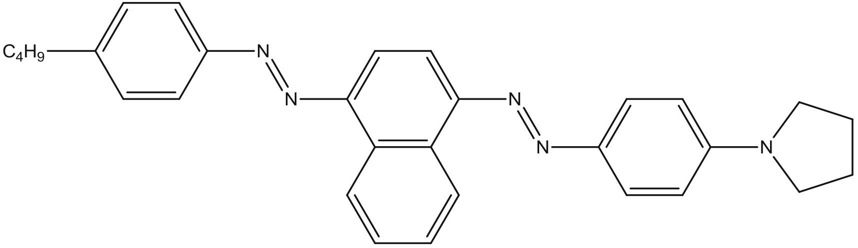
Phthalein dyes are traditionally used for color-change [76]. The use of methanesulfonic acid offers an elegant, one-pot synthesis method for phthalein dyes. Condensation of two equivalents of phenol or substituted phenols with phthalic anhydride in the presence of methanesulfonic acid under anhydrous condition yielded phthalein dyes [77] as shown in Scheme 81.

Liquid Crystal Dyes

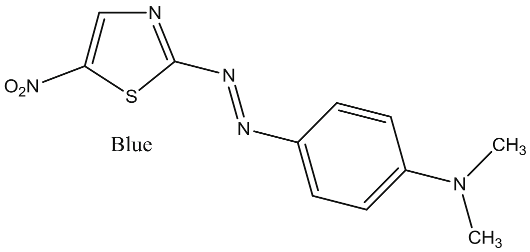
Liquid crystal displays (LCDs) are used in digital watches, clocks, calculators, laptop computers, game displays, and display panels for cars and airplanes. LCDs devoid of dyes are defective in several respects, such as the color contrast is unsatisfactory gray, the angle of vision is limited, and troublesome polarizers are required. Incorporating suitable dyes into the LCDs overcome these disadvantages. Thus, a whole range of highly desirable color contrast is possible, the angle of vision is widened, and the need for polarizers is eliminated. Dyes for liquid crystals must be highly pure, non-ionic, soluble, and compatible with liquid crystals; have a high order parameter; and produce the correct viscosity for a rapid response rate. Originally, azo dyes were used for liquid crystals; however, some azo dyes show poor photostability. The liquid crystal dyes should have high photostability; otherwise, they will fade too quickly. Anthraquinone dyes demonstrate high photostability and are used as liquid crystal dyes. The representative examples of liquid crystal dyes based on azo and anthraquinone chromophores [78, 79] are as shown below.



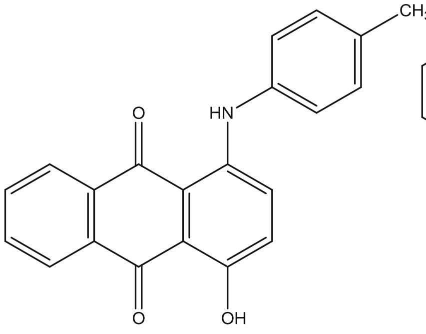
Orange



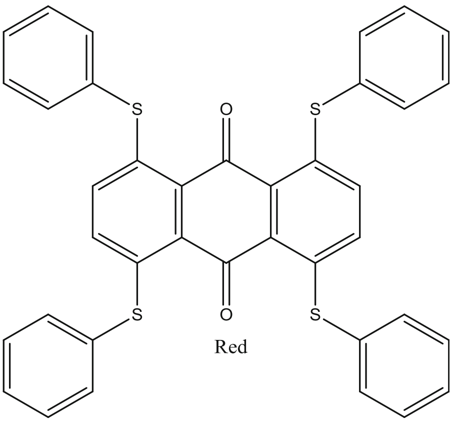
Magenta



Blue



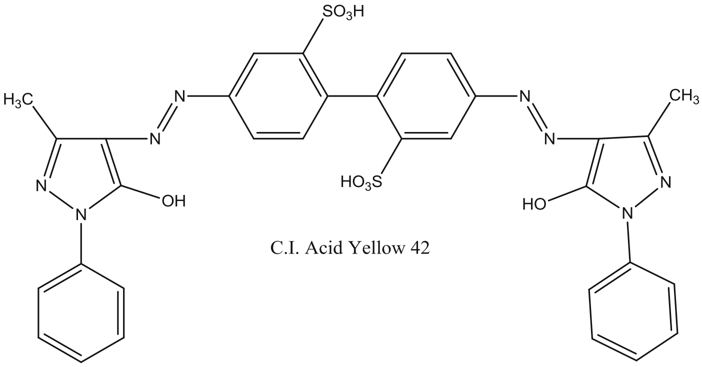
Blue



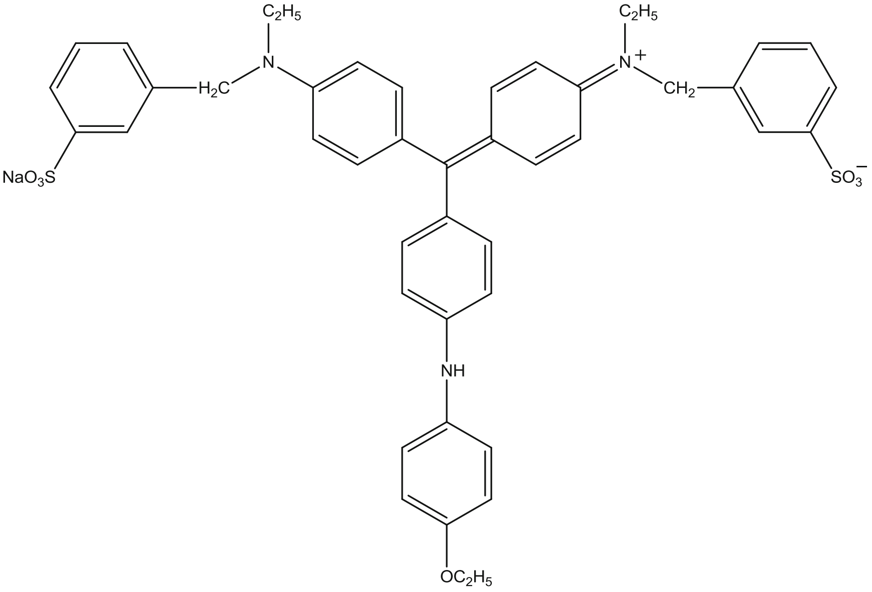
Red

Color Filter Dyes for Displays and Sensors

Color filters are used in displays, sensors, and charge coupled devices (CCDs). The use of dyes in color filters is another rapidly expanding field of research. A color filter (CF) is one of the most important elements for colored liquid crystal displays (LCDs) because it directly defines the color image quality of the display. Color filters are used in conjunction with liquid crystals and thin-film transistors to produce full-color flat-screen displays, such as flat-screen televisions. The details of color filters with reference to the concept, structure, requirements, manufacturing methods, materials, and processes along with black matrix are summarized in a review [80]. The dyes used for color filter are water soluble, should have good fastness properties, and are capable of dyeing substrates. The dyes used are acid, direct, and reactive dyes. The color filters fabricated using dyes are characterized by high transmittance and good color purity. Dyeing method generates color filters with fine resolution, good chromaticities, and excellent dyeing properties. The representative examples of color filter dyes based on azo and triphenylmethane chromophores are as shown below.



C.I. Acid Yellow 42



C.I. Acid Blue 83

Ink-Jet Dyes

Ink-jet printing involves squirting droplets of ink onto a substrate (paper or plastic) to produce an image [81]. It is one of the fastest growing digital technologies in the market. Ink-jet technology is divided into two types: continuous ink-jet and drop-on-demand ink-jet.

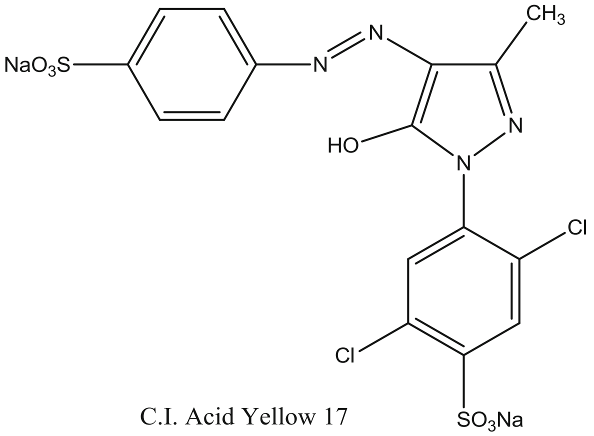
Continuous Ink-Jet Technology

A continuous stream of ink droplets is ejected from a nozzle. Some of these droplets are targeted at the paper to form the image while the remainder are collected in a gutter and either recycled or rejected. In continuous ink-jet technology, two designs are possible. In the first design, the charged ink droplets are deflected on to the paper to form the image and the uncharged droplets are collected in gutter. This is called raster scan continuous ink-jet system. In the second design, the uncharged ink droplets are deflected on to the paper to form the image and the charged droplets are collected in gutter. This is called binary continuous ink-jet system. Continuous ink-jet system is more suited to industrial applications such as the printing of rough and irregular surfaces.

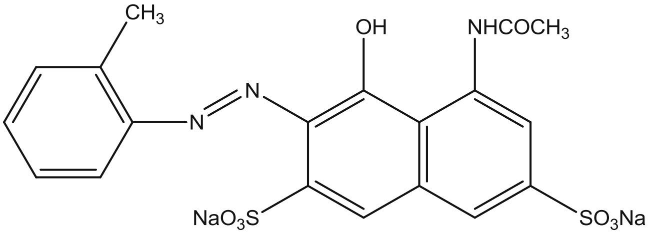
Drop-on-Demand Ink-Jet Technology

All the ink droplets are used to form the image; none are wasted. Ink droplets are only ejected where a dot is required on the substrate; that is, they are produced "on demand." The droplets are not charged. Hence, there is no deflection involved. Instead, the droplets are "fired" in a straight line to the desired position on the paper. The printhead in drop-on-demand ink-jet printing should be as close as possible to the substrate surface so that the ink droplets travel as short a distance as possible to produce accurate images. Drop-on-demand ink-jet system is suited to printing on plain, smooth substrates where higher quality is required.

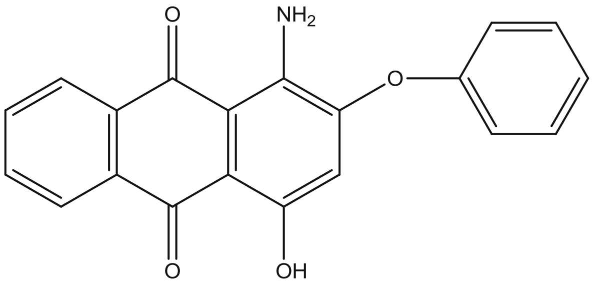
The dyes used for ink-jet formulations offer many advantages such as large choice, high color brilliance, large color gamut, transparency, ease of making ink formulation, and high abrasion resistance and produce stable inks. The dyes used for ink-jet are in four shades such as yellow, magenta, cyan, and black. The dyes are divided into two types: dyes for aqueous-based ink-jet systems and dyes for solvent/hot melt-based ink-jet systems. Dyes for aqueous-based ink-jet systems are acid, food, and direct dyes. Dyes for solvent/hot melt-based ink-jet systems are disperse and solvent dyes. The representative examples of ink-jet dyes based on azo and anthraquinone chromophores are as shown below.



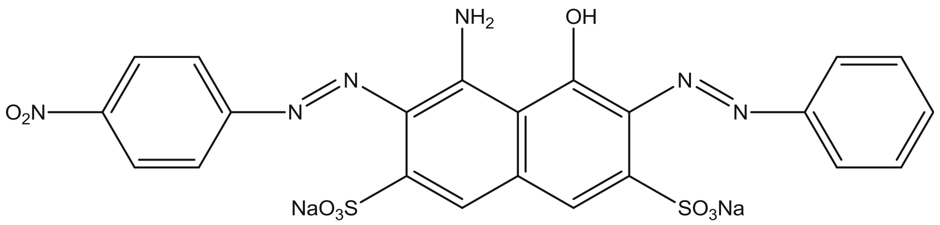
C.I. Acid Yellow 17



C.I. Acid Red 35



C.I. Disperse Red 60

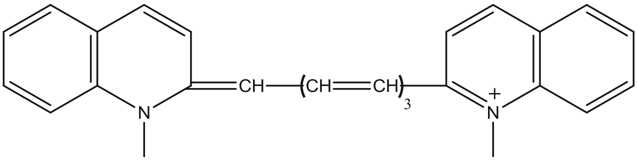


C.I. Acid Black 1

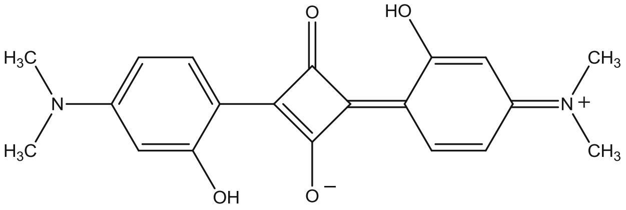
Infrared Absorbing Dyes

Infrared absorbers absorb infrared radiation. The infrared region of the electromagnetic spectrum lies between the visible region and the microwave region. Infrared radiation is normally considered as comprising the wavelengths from 700 to 10,000 nm, which can be subdivided into near, medium, and far-infrared regions. Infrared radiation produces heat when absorbed. Infrared absorbers are being designed to block out this heat and to utilize this heat.

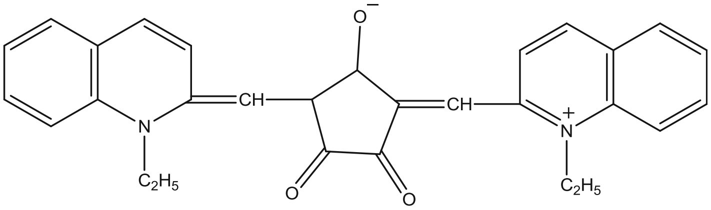
Infrared absorbing dyes are nitroso, cyanine, nigrosine, triphenylmethane, squariliums, croconiums, metal complex, quinones, phthalocyanines, azo, and indoanilines [82]. The infrared absorbing dyes based on small organic molecules that function in the near-infrared (NIR) region are of great current interest in chemical biology. They allow for imaging with minimum autofluorescence from biological samples, reduced light scattering, and high tissue penetration. The design strategies, properties, and bioimaging applications of NIR dyes are summarized [83]. NIR dyes that can preferentially accumulate in tumor cells without the need of chemical conjugation to tumor-targeting ligands have been developed and these dyes have shown unique optical and pharmaceutical properties. A concise overview of newly developed NIR dyes and their potential applications in cancer targeting and imaging is reported [84]. The representative examples of infrared absorbing dyes are cyanine, squarilium, croconium, and naphthoquinone as shown below.



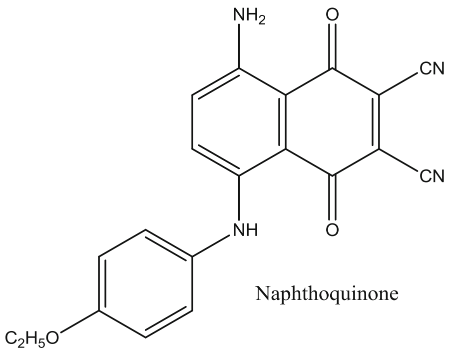
Cyanine



Squarilium



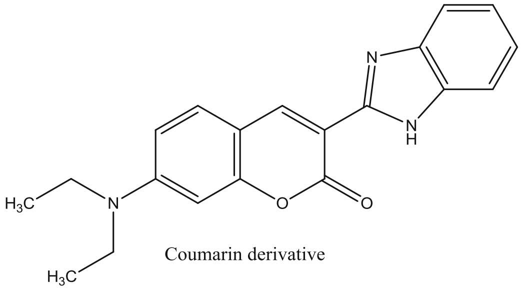
Croconium



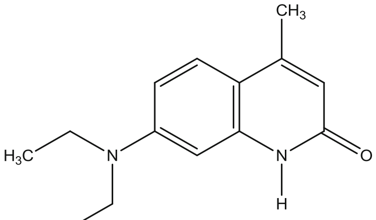
Naphthoquinone

Laser Dyes

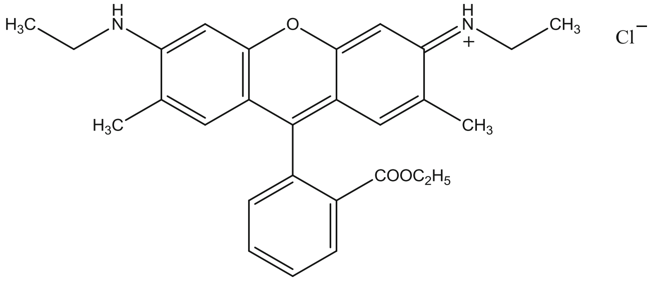
Laser dyes cover the entire visible and near-infrared spectrum from <400 to 1000 nm and have a far greater tenability than the inorganic lasers. Dye lasers emit a broad band of radiation in contrast to inorganic lasers, which emit very narrow bands. Each laser dye is effective only within a 50–100 nm range. Laser dyes have to be very pure since impurities frequently quench laser output. These dyes are usually dissolved in a very pure solvent such as water, ethanol, and N, N-dimethylformamide (DMF) and the choice of solvent can affect the strength and position of the laser output. The solvent therefore gives a further parameter for control. Chemically, laser dyes are cyanines, coumarins, quinolones, xanthenes, phthalocyanines, triarylmethanes, acridines, and azines [85, 86]. The representative examples of laser dyes are coumarin derivative, quinolone derivative, and Rhodamine 6G as shown below.



Coumarin derivative



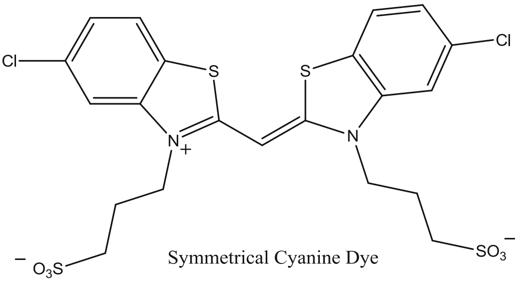
Quinoline derivative



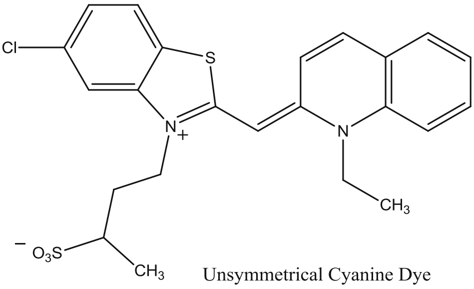
Rhodamine 6G

Photographic Dyes

Dyes are used in photography for two fundamental purposes. The first is for the sensitization of photographic materials, i.e., silver halide crystals from 400 to 1300 nm. The second purpose is for producing color images [87]. Dyes have been developed which can sensitize silver halide emulsions throughout the visible spectrum from 400 to 700 nm and up to 1300 nm in the infrared region. Adsorption to silver halide surface is one of the most important requirements for a sensitizing dye. Intimate contact with the silver surface facilitates electron transfer. It is important that the dyes are not easily displaced from silver surfaces in order to make stable films with predictable photographic properties. The dyes must also have appropriate redox properties to function properly as sensitizers. If the dyes are oxidized too easily in the ground state, silver atoms can be prematurely reduced causing photographic fog. Photographic fog causes a loss of signal-to-noise ratio and degrades image quality. Cyanines are most widely used sensitizing dyes. The representative examples of symmetrical and unsymmetrical cyanine dyes are as shown below.

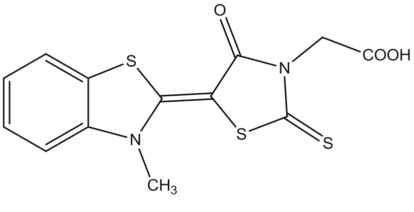


Symmetrical Cyanine Dye

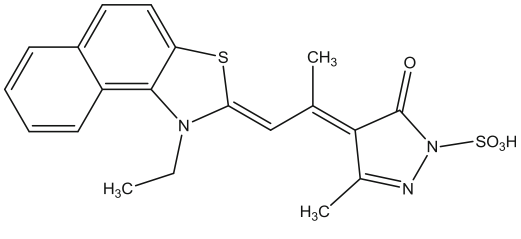


Unsymmetrical Cyanine Dye

The merocyanine dyes are also valuable class of photographic sensitizers. They are soluble in nonpolar solvents than the ionic cyanine dyes because of their nonionic nature. The representative examples of merocyanine dyes as blue sensitizer and green sensitizer are as shown below.

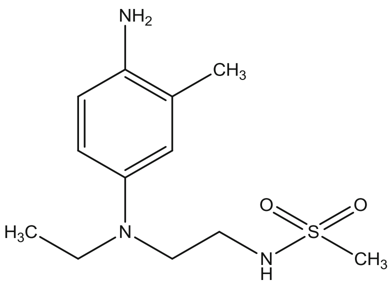


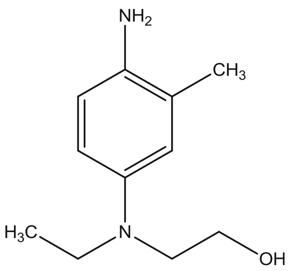
Blue sensitizer



Green sensitizer

In color photography, N,N-dialkylbenzene-1,4-diamines are used as developers. They are directly incorporated into the alkaline-processing fluid. The methyl group in 2-position is important in preventing side reactions and enhancing the formation of the desired dye. The representative examples of color developers are as shown below.





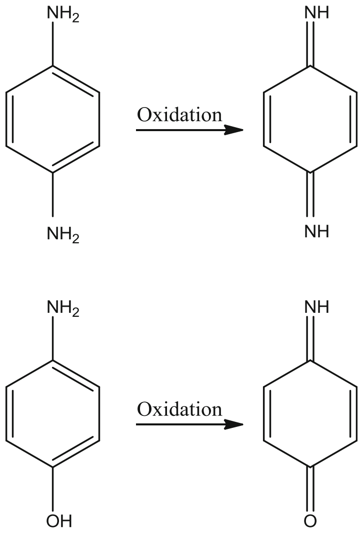
Hair Dyes

The use of coloring matters on human hair may well be older than their application to apparel and furnishings. Hair dyes are divided into three categories depending on their fastness and types of dyes used: permanent hair dyes, semi-permanent hair dyes, and temporary hair dyes. A permanent hair dye lasts through any number of washings as well as permanent waving. A semi-permanent hair dye is removed after two to ten washings and a temporary hair dye is largely eliminated after one washing [88–92].

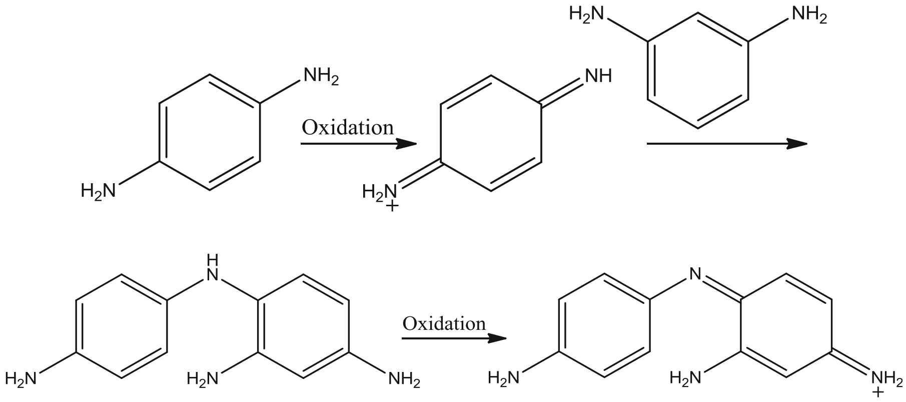
The best method of achieving a permanent hair color is the use of oxidation hair dyes. The dyes are produced inside the hairs from color precursors by oxidation with hydrogen peroxide in alkaline solution. Hairs are uniformly colored based on a suitable choice of intermediates. A primary intermediate, i.e., a para-substituted aromatic compound such as a derivative of 1,4-diaminobenzene or of 4-aminophenol, is oxidized to quinonediimine or quinonemonoimine, respectively, as shown in Scheme 82.

This imine then reacts with a secondary intermediate, called coupler, which is a meta-substituted compound such as a derivative of 1,3-diaminobenzene, 3-aminophenol, or resorcinol, followed by another oxidation step yieling indo, phenazine, and oxazine dyes, which are three times the size of the precursors. The mechanism of coupling reaction is shown in Scheme 83.

The most commonly used primary intermediates are 1,4-diaminobenzene, 2,5-diaminotoluene, 4-amino-3-methylphenol, N,N-bis-(hydroxyethyl)-p-phenylenediamine, and 4,5-diamino-1-methylpyrazole. The most commonly used couplers are 1,3-diaminobenzene, 3-aminophenol, 5-amino-2-methylphenol, resorcinol, 1-naphthol, 4-chlororesorcinol, 2-methylresorcinol, and



Scheme 82 First step in color formation in oxidative dyeing



Scheme 83 Mechanism of oxidative coupling of 1,4-diaminobenzene (primary intermediate) with 1,3-diaminobenzene (coupler)

2,4-diaminophenoxyethanol. The permanent hair colorants are generally sold as two-component kit. One component comprises the mixtures of dye precursors in an alkaline soap or syndet base and the second component is a stabilized solution of hydrogen peroxide. In some cases, peroxide is provided as powder such as urea peroxide or melamine peroxide. Addition of a base is necessary to give a pH range of 9.0–9.7.

Semi-permanent hair dyes are products which employ sparingly soluble, low-molecular-weight, direct dyes which can diffuse into the hair fibers under ambient conditions and which can produce an effect which lasts up to ten shampoo treatments. The most commonly used dyes are aminonitrophenols, nitrophenylenediamines, aminoanthraquinones, and azo. The semi-permanent hair dyes are usually presented as lotions intended for direct application to the hairs. The dyes are dissolved or dispersed in an oil-in-water emulsion containing non-ionic surfactants and amines to give a pH in the range of 8.0–9.5.

In contrast to permanent hair dyes and semi-permanent hair dyes, the temporary hair dyes are intended to wash out completely when the hair is shampooed. Consequently, the products are applied as rinses, lotions, gels, spray-on products, or foams. The most commonly used dyes are acid dyes and basic dyes, but also sometimes solvent dyes.

Food Dyes

Coloring fresh food is not permitted as a matter of principle. A synthetic dye is permitted for dyeing food only if thorough toxicological studies reveal no danger of toxic effects to the consumer. Coloring is generally added to food at a very early stage in processing. Food dyes must be stable to heating, cooling, acid, and oxygen; during storage; and upon exposure to light. Water-soluble dyes are mainly used as food colorants. Most synthetic dyes, which are commonly used in food, should be approved for food coloring in the United States, Europe, and Japan. The Federal Food, Drugs and Cosmetics Act provides that foods, drugs, cosmetics, and some medical devices are adulterated if they contain color additives that have not been approved safe to the satisfaction of Food and Drug Administration (FDA) for the particular use. A color additive is a dye, pigment, or other source, which imparts a color when added or applied to foods, drugs, cosmetics, or the human body. The main uses of food coloring are in beverages, cakes, confectionaries, cheese, fruit-based products, and fish products [93].

Regulations 21 CFR, Parts 73, 74, and 81 list the approved color additives and the conditions under which they may be safely used, including the amounts that may be used when limitations are necessary. Colorants permitted in food along

Table 7 Colorants permitted in food along with CAS number and Colour Index number

Chemical name	CAS number	Colour Index Number
FD&C Blue 1	3844-45-9	42090
FD&C Blue 2	860-22-0	73015
FD&C Green 3	2353-45-9	42053
FD&C Red 3	16423-68-0	45430
FD&C Red 40	25956-17-6	16035
FD&C Yellow 5	1934-21-0	19140
FD&C Yellow 6	2783-94-0	15985

with CAS number and Colour Index Number are given in Table 7.

Biomedical Dyes

The great majority of substances used in biological staining are dyes. The science of biological staining has been of immense importance in clinical diagnosis, pathology, and plant biology. Identification of cell types in samples of dispersed cells constitutes a major area of diagnostic use of dyes. In addition to the widespread use of immunostaining in cytogenetics and chromosome banding is still carried out with dyes. Hematology and flow cytometry in counting and study of blood cells utilize dyes. Healthy and diseased tissues are regularly recognized by means of staining techniques using dyes. Fluorescent dyes are used for staining cells, cell organelles, and nucleic acids. Photodynamic therapy in combination with dyes is commonly used in diagnosis, detection, and treatment of cancer. Dyes possess antimicrobial properties even in the absence of light. Biological Stain Commission-certified dyes are Acid Fuchsin, Alcian Blue 8GX, Alizarin Red S, Aniline Blue, Auramine O, Azure A, Azure B, Basic Fuchsin, Bismark Brown Y, Brilliant Cresyl Blue, Brilliant Green, Carmine, Congo Red, Cresyl Violet acetate, Cresyl Violet, Eosin B, Eosin Y, Erythrosine, Ethyl Eosin, Fast Green FCF, Giemsa stain, Hematoxylin, Indigo Carmine, Janus Green B, Light Green SF Yellowish, Malachite Green oxalate salt, Methylene Blue trihydrate, Methylene Violet, Methyl Green, Methyl Orange, Methyl Violet 2B, Neutral Red, Nigrosin, Nile Blue A, Oil Red O, Orange G, Orcein, Pararosaniline hydrochloride, Phloxine B, Pyronine B, Pyronin Y, Resazurin sodium salt, Rose Bengal, Safranin O, Sudan Black B, Sudan III, Sudan IV, Thionin and Toluidine Blue O [93–95].

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