DYES AND DYE INTERMEDIATES

1. Introduction

The first synthetic dye, Mauveine, was discovered by Perkin in 1856. Hence the dyestuffs industry can rightly be described as mature. However, it remains a vibrant, challenging industry requiring a continuous stream of new products because of the quickly changing world in which we live. The early dyes industry saw the discovery of the principal dye chromogens (the basic arrangement of

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atoms responsible for the color of a dye). Indeed apart from one or two notable exceptions, all the dye types used today were discovered in the nineteenth century (1). The introduction of the synthetic fibers, nylon, polyester, and polyacrylonitrile during the period 1930–1950, produced the next significant challenge. The discovery of reactive dyes in 1956 heralded a big breakthrough in the dyeing of cotton; intensive research into reactive dyes followed over the next two decades and, indeed, is still continuing today (1) (see DYES, REACTIVE). The oil crisis in the early 1970s, which resulted in a steep increase in the prices of raw materials for dyes, created a drive for more cost-effective dyes, both by improving the efficiency of the manufacturing processes and by replacing tinctorially weak chromogens, such as anthraquinone, with tinctorially stronger chromogens, such as azo and benzodifuranone. These themes are still important and ongoing, as are the current themes of product safety, quality, and protection of the environment. There is also considerable activity in dyes for high technology applications, especially for the electronics and reprographics industries (see DYES, ANTHRAQUINONE).

The scale and growth of the dyes industry is inextricably linked to that of the textile industry. World textile production has grown steadily to an estimated 35 million tons in 1990 (2,3). The two most important textile fibers are cotton, the largest, and polyester. Consequently, dye manufacturers tend to concentrate their efforts on producing dyes for these two fibers. The estimated world production of dyes in 1990 was 1 million tons (2,3). This figure is significantly smaller than that for textile fiber because a little dye goes a long way. For example, 1 t of dye is sufficient to color 16,650 cars or 42,000 suits (3).

Perkin, an Englishman, working under a German professor, Hoffman, discovered the first synthetic dye, and even today the geographical focus of dye production lies in Germany (BASF, Bayer, Hoechst), England (Zeneca), and Switzerland (CIBA-GEIGY and Sandoz). Far Eastern countries, such as Japan, Korea, and Taiwan, and Third World countries, such as India, Brazil, and Mexico, also produce dyes.

2. Classification Systems for Dyes

Dyes may be classified according to chemical structure or by their usage or application method. The former approach is adopted by practicing dye chemists who use terms such as azo dyes, anthraquinone dyes, and phthalocyanine dyes. The latter approach is used predominantly by the dye user, the dye technologist, who speaks of reactive dyes for cotton and disperse dyes for polyester. Very often, both terminologies are used, for example, an azo disperse dye for polyester and a phthalocyanine reactive dye for cotton.

2.1. Chemical Classification. The most appropriate system for the classification of dyes is by chemical structure, which has many advantages. First, it readily identifies dyes as belonging to a group that has characteristic properties, for example, azo dyes (strong and cost-effective) and anthraquinone dyes (weak and expensive). Secondly, there are a manageable number of chemical groups (about a dozen). Most importantly, it is the classification used most widely by both the synthetic dye chemist and the dye technologist. Thus, both chemists and technologists can readily identify with phrases such as an azo yellow, an anthraquinone red, and a phthalocyanine blue.

The classification given in this article maintains the backbone of the Colour Index classification, but attempts to simplify and update it. This is done by showing the structural interrelationships of dyes that are given separate classes by the Colour Index, and the classification is chosen to highlight some of the more recent discoveries in dye chemistry (4).

2.2. Usage Classification.

It is advantageous to consider the classification of dyes by use or method of application before considering chemical structures in detail because of dye nomenclature and jargon that arises from this system.

Classification by usage or application is the principal system adopted by the Colour Index (5). Because the most important textile fibers are cotton (qv) and polyester, the most important dye types are those used for dyeing these two fibers, including polyester–cotton blends (see FIBERS, POLYESTER). Other textile fibers include nylon, polyacrylonitrile, and cellulose acetate (see FIBERS, ACRYLIC; FIBERS, CELLULOSE ESTERS; FIBERS, POLYAMIDE).

3. Classification of Dyes by Use or Application Method

The classification of dyes according to their usage is summarized in Table 1, which is arranged according to the CI application classification. It shows the principal substrates, the methods of application, and the representative chemical types for each application class.

Table 1. **Usage Classification of Dyes**

Class	Principal substrates	Method of application	Chemical types[a]
acid	nylon, wool, silk, paper, inks, and leather	usually from neutral to acidic dyebaths	azo, including premetallized anthraquinone, triphenylmethane, azine, xanthene, nitro, and nitroso
azoic components and compositions	cotton, rayon, cellulose acetate, and polyester	fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt	azo
basic	paper, polyacrylonitrile-modified nylon, polyester, and inks	applied from acidic dyebaths	diazacarbocyanine cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
direct	cotton, rayon, paper, leather, and nylon	applied from neutral or slightly alkaline baths containing additional electrolyte	azo, phthalocyanine, stilbene, and oxazine

Table 1 (*Continued*)

Class	Principal substrates	Method of application	Chemical types[a]
disperse	polyester, polyamide, acetate, acrylic, and plastics	fine aqueous dispersions often applied by high temperature–pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	azo, anthraquinone, styryl, nitro, and benzodifuranone
fluorescent brighteners[b]	soaps and detergents, all fibers, oils, paints, and plastics[c]	from solution, dispersion, or suspension in a mass	stilbene, pyrazoles, coumarin, and naphthalimides
food, drug, and cosmetic[d]	foods, drugs, and cosmetics		azo, anthraquinone, carotenoid, and triarylmethane
mordant[e]	wool, leather, and anodized aluminum	applied in conjunction with chelating Cr salts	azo and anthraquinone
natural[f]	food	applied as mordant, vat, solvent, or direct and acid dyes	anthraquinone, flavonols, flavones, indigoids, chroman
oxidation bases	hair, fur, and cotton	aromatic amines and phenols oxidized on the substrate	aniline black and indeterminate structures
pigments[g]	paints, inks, plastics, and textiles	printing on the fiber with resin binder or dispersion in the mass	azo, basic, phthalocyanine, quinacridone, and indigoid
reactive[h]	cotton, wool, silk, and nylon	reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	azo, anthraquinone, phthalocyanine, formazan, oxazine, and basic
solvent	plastics, gasoline, varnish, lacquer, stains, inks, fats, oils, and waxes	dissolution in the substrate	azo, triphenylmethane, anthraquinone, and phthalocyanine
sulfur	cotton and rayon	aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	indeterminate structures
vat	cotton, rayon, and wool	water-insoluble dyes solubilized by reducing with sodium hydrosulfite, then exhausted on fiber and reoxidized	anthraquinone (including polycyclic quinones) and indigoids

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[a] *Encyclopedia* articles on specific chemical types of dyes are AZINE DYES; AZO DYES; CYANINE DYES; DYES, ANTHRAQUINONE; PHTHALOCYANINE COMPOUNDS; POLYMETHINE DYES; STILBENE DYES; SULFUR DYES; THIAZOLE DYES; TRIPHENYLMETHANE AND RELATED DYES; XANTHENE DYES.

[b] See FLUORESCENT WHITENING AGENTS.

[c] See COLORANTS FOR PLASTICS.

[d] See COLORANTS FOR FOODS, DRUGS, COSMETICS, AND MEDICAL DEVICES.

[e] See DYES, APPLICATIONS AND EVALUATION.

[f] See DYES, NATURAL.

[g] See PAINT; PIGMENTS; INKS.

[h] See DYES, REACTIVE.

Although not shown in Table 1, dyes are also being used in high technology applications, such as in the medical, electronics, and especially the reprographics industries. For example, they are used in electrophotography (qv) (photocopying and laser printing) in both the toner and the organic photoconductor, in ink jet printing, and in direct and thermal transfer printing (6). As in traditional applications, azo dyes predominate; phthalocyanine, anthraquinone, xanthene, and triphenylmethane dyes are also used. These applications are low volume (tens of kg up to several hundred t per annum) and high added value (hundreds of dollars to several thousand dollars per kg), with high growth rates (up to 60%).

3.1. Reactive Dyes. These dyes form a covalent bond with the fiber, usually cotton, although they are used to a small extent with wool and nylon. This class of dyes, first introduced commercially in 1956 by ICI, made it possible to achieve extremely high washfastness properties by relatively simple dyeing methods. A marked advantage of reactive dyes over direct dyes is that their chemical structures are much simpler, their absorption spectra show narrower absorption bands, and the dyeings are brighter. The principal chemical classes of reactive dyes are azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone (see DYES, REACTIVE).

3.2. Direct Dyes. These water-soluble anionic dyes, when dyed from aqueous solution in the presence of electrolytes, are substantive to, ie, have high affinity for, cellulosic fibers. The principal use is the dyeing of cotton and regenerated cellulose, paper, leather, and, to a lesser extent, nylon. Most of the dyes in this class are azo compounds with some stilbenes, phthalocyanines, and oxazines. After-treatments, frequently given to the dyed material to improve washfastness properties, include chelation with salts of metals (usually copper or chromium), and treatment with formaldehyde or a cationic dye-complexing resin.

3.3. Vat Dyes. These water-insoluble dyes are applied mainly to cellulosic fibers as soluble leuco-salts after reduction in an alkaline bath, usually with sodium hydrosulfite. Following exhaustion onto the fiber, the leuco forms are reoxidized to the insoluble keto forms and aftertreated, usually by soaping, to redevelop the crystal structure. The principal chemical classes of vat dyes are anthraquinone and indigoid.

3.4. Sulfur Dyes. These dyes are applied to cotton from an alkaline-reducing bath with sodium sulfide as the reducing agent. Numerically this is a relatively small group. However, the low cost and good washfastness properties of the dyeings make this class important from an economic standpoint (see SULFUR DYES).

3.5. Disperse Dyes. These are substantially water-insoluble nonionic dyes for application to hydrophobic fibers from aqueous dispersion. They are used predominantly on polyester and to a lesser extent on nylon, cellulose, cellulose acetate, and acrylic fibers. Thermal transfer printing, in which disperse dyes are printed onto paper and subsequently transferred to the fiber by a dry-heat process, represents a niche market for selected members of this class. They are also used in the Dye Diffusion Thermal Transfer (D2T2) process for electronic photography (6) (see ELECTROPHOTOGRAPHY).

3.6. Basic Dyes. These water-soluble cationic dyes are applied to paper, polyacrylonitrile (eg, Dralon), modified nylons, and modified polyesters. Their original use was for silk, wool, and tannin-mordanted cotton when brightness of shade was more important than fastness to light and washing. Basic dyes are water-soluble, and yield colored cations in solution. For this reason they are frequently referred to as cationic dyes. The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine. Some basic dyes show biological activity and are used in medicine as antiseptics (see DISINFECTANTS AND ANTISEPTICS).

3.7. Solvent Dyes.

These water-insoluble dyes are devoid of polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. They are used for coloring plastics, gasoline, oils, and waxes. The dyes are predominantly azo and anthraquinone, but phthalocyanines and triarylmethane dyes are also used.

3.8. Acid Dyes.

These water-soluble anionic dyes are applied to nylon, wool, silk, and modified acrylics. They are also used to some extent for paper, leather, food, and cosmetics. The original members of this class all had one or more sulfonic or carboxylic acid groups in their molecules. This characteristic probably gave the class its name. Chemically, the acid dyes consist of azo (including preformed metal complexes), anthraquinone, and triarylmethane compounds with a few azine, xanthene, ketone imine, nitro, nitroso, and quinophthalone compounds.

4. Nomenclature of Dyes

Dyes are named either by their commercial trade name or by their Colour Index (CI) name. In the Colour Index (5) these are cross-referenced.

The commercial names of dyes are usually made up of three parts. The first is a trademark used by the particular manufacturer to designate both the manufacturer and the class of dye, the second is the color, and the third is a series of letters and numbers used as a code by the manufacturer to define more precisely the hue, and also to indicate important properties the dye possesses. The code letters used by different manufacturers are not standardized. The most common letters used to designate hue are R for reddish, B for bluish, and G for greenish shades. Some of the more important letters used to denote the dyeings and fastness properties of dyes are W for washfastness and E for exhaust dyes. For solvent and disperse dyes, the heatfastness of the dye is denoted by letters A, B, C, or D, A being the lowest level of heatfastness and D being the highest. In reactive dyes for cotton, M denotes a warm (ca 40°C) dyeing dye and H a hot (ca 80°C) dyeing dye. Examples that follow illustrate the use of these letters.

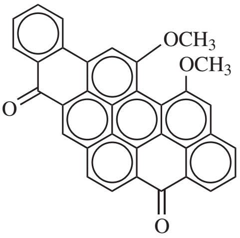
Consider Dispersol Yellow B-6G. Dispersol is the Zeneca trade name for its range of disperse dyes for polyester. Therefore, it reveals the manufacturer and the usage. Yellow denotes the main color of the dye. “B” denotes its heatfastness, ie, rather low, and 6G denotes that it is six steps of green away from a neutral yellow, so it is a very greenish yellow, ie, a lemon yellow.

In the name Procion Red H-E 7B, Procion is the Zeneca trade name for its range of reactive dyes for cotton. Red denotes the main color of the dye. H-E denotes the dye to be hot dyeing and an exhaust dye (high fixation), and 7B denotes it to be a very bluish red dye, ie, a magenta.

There are instances in which one manufacturer may designate a bluish red dye as Red 4B and another manufacturer uses Violet 2R for the same dye. To resolve such a problem the manufacturers' pattern leaflets should be consulted. These show actual dyed pieces of cloth so the colors of the dyes in question can be compared directly in the actual application. Alternatively, colors can be specified in terms of color space coordinates. The Cielab system is becoming the standard; in this system the color of a dye is defined by three numbers, the L, a, and b coordinates (see COLOR).

The CI name for a dye is derived from the application class to which the dye belongs, the color or hue of the dye, and a sequential number, eg, CI Acid Yellow 3, CI Acid Red 266, CI Basic Blue 41, and CI Vat Black 7. A five digit CI number is assigned to a dye when its chemical structure has been made known by the manufacturer. The following example illustrates these points, where CA indicates *Chemical Abstracts* and CI *Colour Index*.

chemical structure:

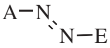


molecular formula:	$C_{36}H_{20}O_4$
CA name:	16,17-dimethoxydinaphtho[1,2,3−*cd*:3′,2′,1′,−*lm*] perylene-5,10-dione
trivial name:	jade green
CI name:	CI Vat Green 1
CI number:	CI 59825
application class:	vat
chemical class:	anthraquinone
CAS Registry Number:	[128-58-5]
commercial names:	Solanthrene Green XBN, Zeneca Specialties Cibanone Brilliant Green, BF, 2BF, BFD, CIBA-GEIGY SA Indanthrene Brilliant, Green, B, FB, Badische Anilin-und Soda-Fabric AG (BASF)

5. Classification of Dyes by Chemical Structure

The two overriding trends in dyestuffs research for many years have been improved cost-effectiveness and increased technical excellence. Improved cost-effectiveness usually means replacing tinctorially weak dyes such as anthraquinone, the second largest class after the azo dyes, with tinctorially stronger dyes such as heterocyclic azos, triphendioxazines, and benzodifuranones. This theme will be pursued throughout this section discussing dyes by chemical structure.

5.1. Azo Dyes. These dyes are by far the most important class, accounting for over 50% of all commercial dyes, and having been studied more than any other class (see AZO DYES). Azo dyes contain at least one azo group (—N=N—) but can contain two (disazo), three (trisazo), or, more rarely, four or more (polyazo) azo groups. The azo group is attached to two radicals of which at least one, but, more usually, both are aromatic. They exist in the trans form where the bond angle is ca 120° and the nitrogen atoms are *sp*^{2} hybridized and may be represented as follows. The designation of A and E groups is consistent with CI usage (5).



In monoazo dyes, the most important type, the A radical often contains electron-accepting groups, and the E radical contains electron-donating groups, particularly hydroxy and amino groups. If the dyes contain only aromatic radicals such as benzene and naphthalene, they are known as carbocyclic azo dyes. If they contain one or more heterocyclic radicals, the dyes are known as heterocyclic azo dyes. Examples of various azo dyes are shown in Figure 1. These illustrate the enormous structural variety possible in azo dyes, particularly with polyazo dyes.

Synthesis. Almost without exception, azo dyes are made by diazotization of a primary aromatic amine followed by coupling of the resultant diazonium salt with an electron-rich nucleophile. The diazotization reaction is carried out by treating the primary aromatic amine with nitrous acid, normally generated *in situ* with hydrochloric acid and sodium nitrite. The nitrous acid nitrosates the amine to generate the *N*-nitroso compound, which tautomerizes to the diazo hydroxide.

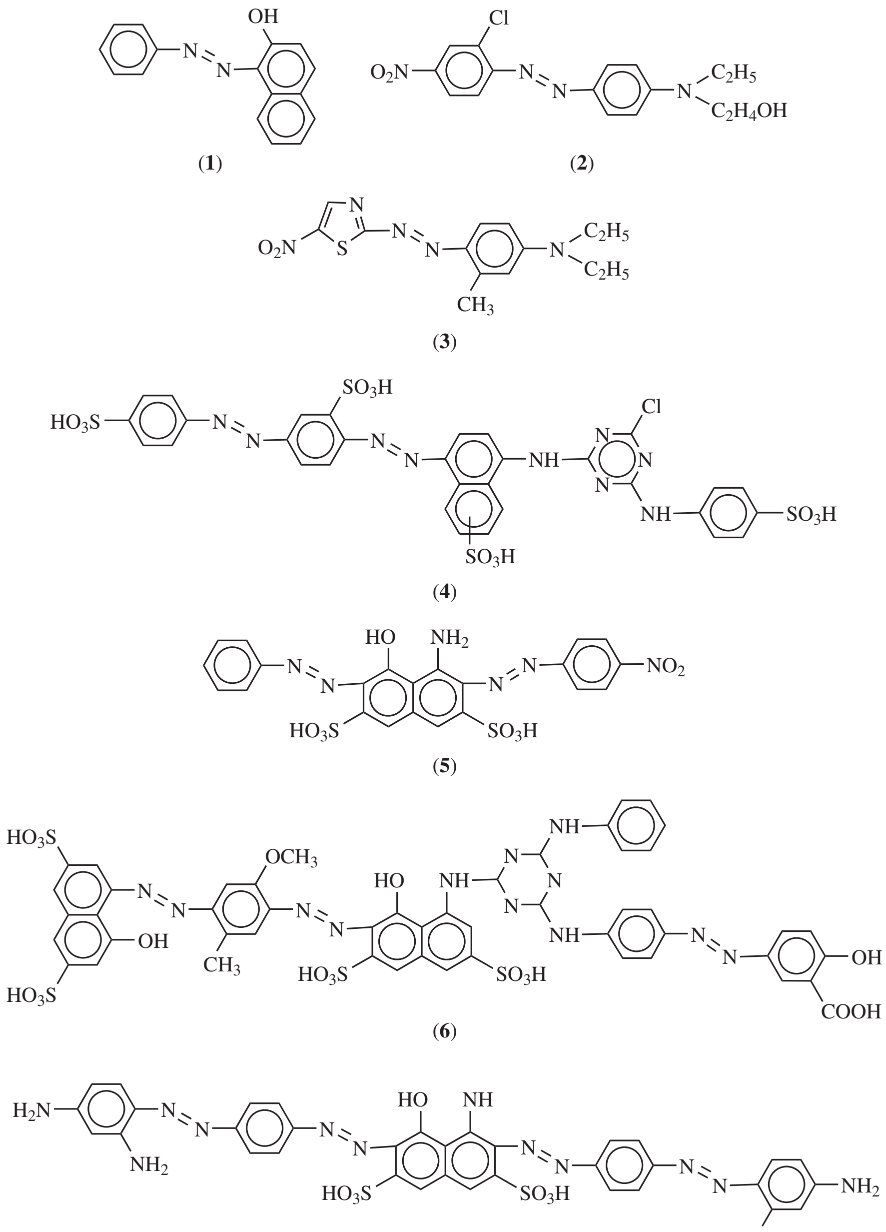
$$\mathrm{Ar{-}NH{-}N{=}O} \rightleftharpoons \mathrm{Ar{-}N{=}N{-}OH}$$

Protonation of the hydroxy group followed by the elimination of water generates the resonance-stabilized diazonium salt.

$$\mathrm{Ar{-}N{=}N^{+}} \longleftrightarrow \mathrm{Ar{-}\overset{+}{N}{\equiv}N}$$

For weakly basic amines, ie, those containing several electron-withdrawing groups, nitrosyl sulfuric acid ($NO^{+}HSO^{-}{}_{4}$) is used as the nitrosating species in sulfuric acid, which may be diluted with phosphoric, acetic, or propionic acid.

A diazonium salt is a weak electrophile, and thus reacts only with highly electron-rich species such as amino and hydroxy compounds. Even hydroxy compounds must be ionized for reaction to occur. Consequently, hydroxy compounds such as phenols and naphthols are coupled in an alkaline medium ($pH \geq pK_a$ of phenol or naphthol; typically pH 7–11), whereas aromatic amines such as *N,N* dialkylamines are coupled in a slightly acid medium, typically pH 1–5. This provides optimum stability for the diazonium salt (stable in acid) without deactivating the nucleophile (protonation of the amine).


(**1**)

(**2**)

(**3**)

(**4**)

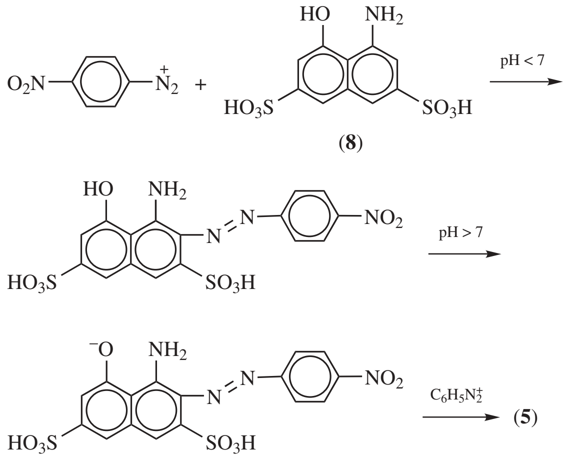
(**5**)

(**6**)

(**7**)

Fig. 1. Azo dyes. (**1**), CI Solvent Yellow 14 [842-07-9] (CI 12055); (**2**), CI Disperse Red 13 [3180-81-2] (CI 11115); (**3**), CI Disperse Blue [70693-64-0]; (**4**), CI Reactive Brown 1 [12238-04-9] (CI 26440); (**5**) CI Acid Black 1 [1064-48-8] (CI 20470) (**6**), CI Direct Green 26 [25780-48-7] (CI 34045); (**7**) CI Direct Black 19 [6428-31-5] (CI 35255).

Coupling components containing both amino and hydroxy groups, such as H-acid (1-amino-8-naphthol-3,6-disulfonic acid) (**8**) [90-20-0], can be coupled stepwise. Coupling is first carried out under acid conditions to effect azo formation in the amino-containing ring. The pH is then raised to ionize the hydroxy group (usually to pH ≥ 7) to effect coupling in the naphtholate ring, with either the same or a different diazonium salt. Doing it in the reverse order fails because the nucleophilicity of the amino group is insufficient to facilitate the second coupling step.



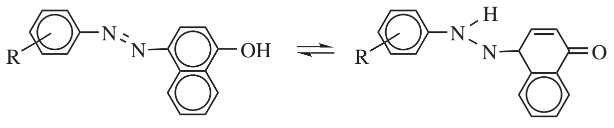
(**8**)

(**5**)

The unusual conditions needed to produce an azo dye, namely, strong acid plus nitrous acid for diazotization, the low temperatures necessary for the unstable diazonium salt to exist, and the presence of electron-rich amino or hydroxy compounds to effect coupling, means that azo dyes have no natural counterparts.

Tautomerism. In theory, azo dyes can undergo tautomerism: azo/hydrazone for hydroxyazo dyes; azo/imino for aminoazo dyes, and azonium/ammonium for protonated azo dyes. A more detailed account of azo dye tautomerism can be found elsewhere (7).

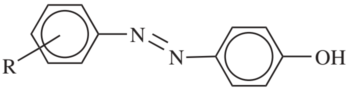
Azo/hydrazone tautomerism was discovered in 1884 (8). The same orange dye was obtained by coupling benzene diazonium chloride with 1-naphthol and by condensing phenylhydrazine with 1,4-naphthoquinone. The expected products were the azo dye (**9**) (R = H) [3651-02-3] and the hydrazone (**10**) (R = H) [19059-71-3]. It was correctly assumed that there was a mobile equilibrium between the two forms, ie, tautomerism.



(**9**) (**10**)

The discovery prompted extensive research into azo/hydrazone tautomerism, a phenomenon which is not only interesting but also extremely important as far as commercial azo dyes are concerned because the tautomers have different colors, different properties, eg, lightfastness, different toxicological properties, and, most importantly, different tinctorial strengths. Since the tinctorial strength of a dye primarily determines its cost-effectiveness, it is desirable that commercial azo dyes should exist in the strongest tautomeric form. This is the hydrazone form.

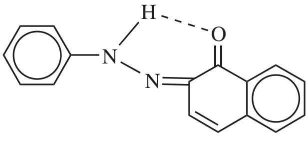
Hydroxyazo dyes vary in the proportion of tautomers present from pure azo tautomer to mixtures of azo and hydrazone tautomers, to pure hydrazone tautomer. Almost all azophenol dyes (**11**) exist totally in the azo form, except for a few special cases (**9**).



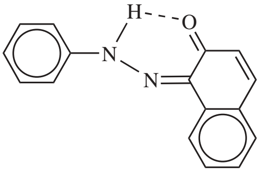
(**11**)

The energies of the azo and hydrazone forms of 4-phenylazo-1-naphthol dyes are similar, so both forms are present. The azo tautomers (**9**) are yellow ($\lambda_{\max} \sim 410$ nm, $\epsilon_{\max} \sim 20,000$) and the hydrazone tautomers (**10**) are orange ($\lambda_{\max} \sim 480$ nm, $\epsilon_{\max} \sim 40,000$). The relative proportions of the tautomers are influenced by both solvent (Fig. 2) and substituents (Fig. 3).

The isomeric 2-phenylazo-1-naphthols (**12**) [1602-36-4] and 1-phenylazo-2-naphthols (**13**) [1602-30-8] exist more in the hydrazone form than the azo form as shown by their uv spectra. Their $\lambda_{\max}$ values are each about 500 nm.



(**12**)



(**13**)

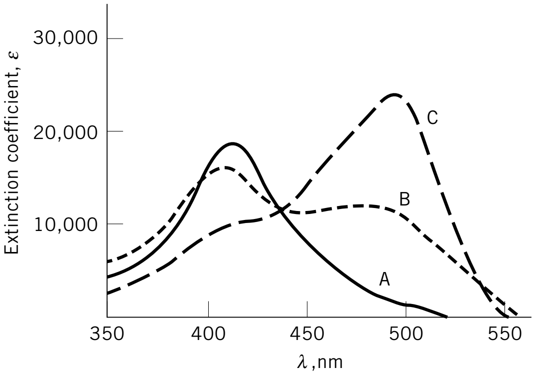


Fig. 2. Effect of solvent on 4-phenylazo-1-naphthol absorption. A, pyridine; B, methanol; C, acetic acid.

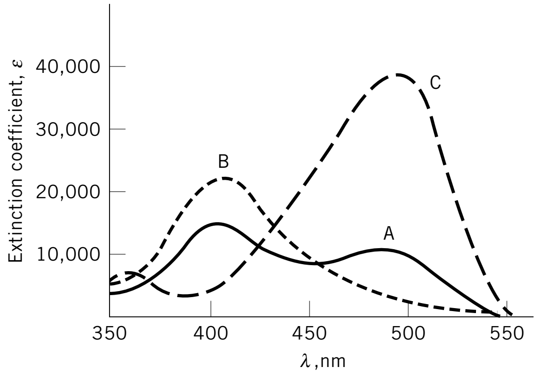
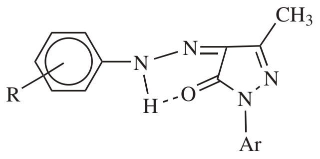


Fig. 3. Electronic effect of substituents in 4-phenylazo-1-naphthol (9). A, R = H; B, R = p–OCH_3; C, R = p–NO_2.

Important classes of dyes that exist totally in the hydrazone form are azopyrazolones (**14**), azopyridones (**15**), and azoacetoacetanilides (**16**).



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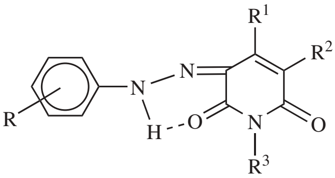
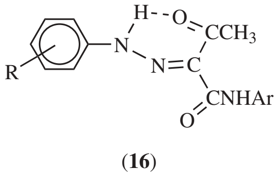
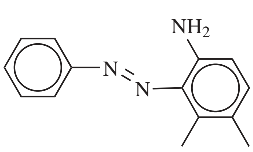


(**15**)

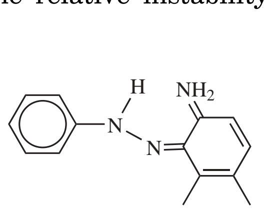


(**16**)

All aminoazo dyes exist exclusively as the azo form; there is no evidence for the imino form. Presumably, a key factor is the relative instability of the imino grouping.

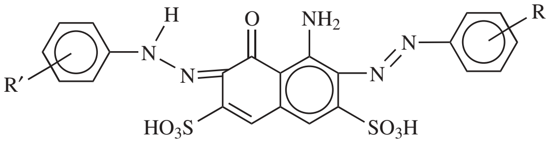


azo



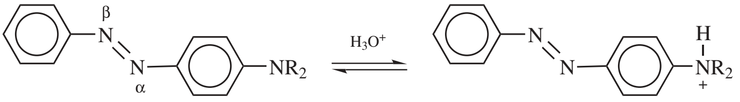
imino

In disazo dyes from aminonaphthols, one group exists as a true azo group and one as a hydrazo group (**17**).



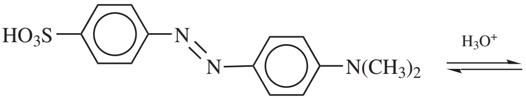
(**17**)

Aminoazo dyes undergo protonation at either the terminal nitrogen atom to give the essentially colorless ammonium tautomer (**18**) ($\lambda_{\max} \sim 325$ nm),

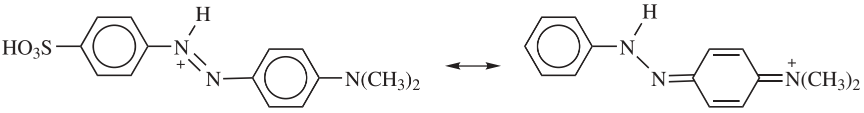


(**18**)

or at the β-nitrogen atom of the azo group to give a resonance-stabilized azonium tautomer (**19**) as shown for methyl orange. The azonium tautomer is brighter, generally more bathochromic and stronger ($\epsilon_{\max} \sim 70,000$) than the neutral azo dye. The azonium tautomers are related to diazahemicycanine dyes used for coloring polyacrylonitrile. The most familiar use of the protonation of azo dyes is in indicator dyes such as methyl orange (**20**) [502-02-3] and methyl red [493-52-7].

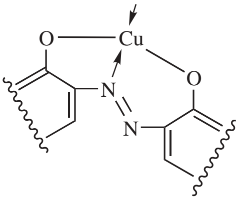


(**20**)
Yellow



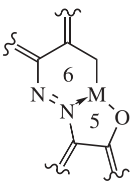
(**19**)
Red

Metallized Azo Dyes. The three metals of importance in azo dyes are copper, chromium, and cobalt. The most important copper dyes are the 1:1 copper(II): azo dye complexes of formula (**21**); they have a planar structure.

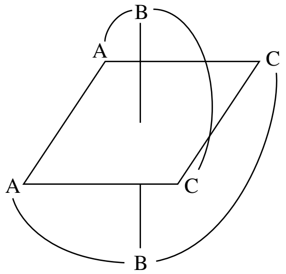


(**21**)

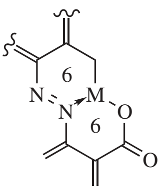
In contrast, chromium(III) and cobalt(III) form 2:1 dye:metal complexes that have nonplanar structures. Geometrical isomerism exists. The *o,o′*-dihydroxyazo dyes (**22**) form the Drew-Pfitzner or *mer* type (**23**) ($A = C = O$) whereas *o*-hydroxy–*o′*-carboxyazo dyes (**24**) form the Pfeiffer-Schetty or *fac* type (**25**), where $A = CO_2$ and $C = O$.



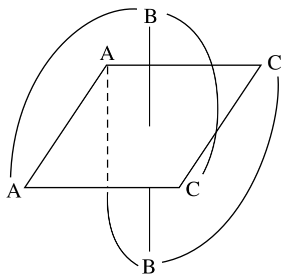
(**22**)



(**23**)



(**24**)



(**25**)

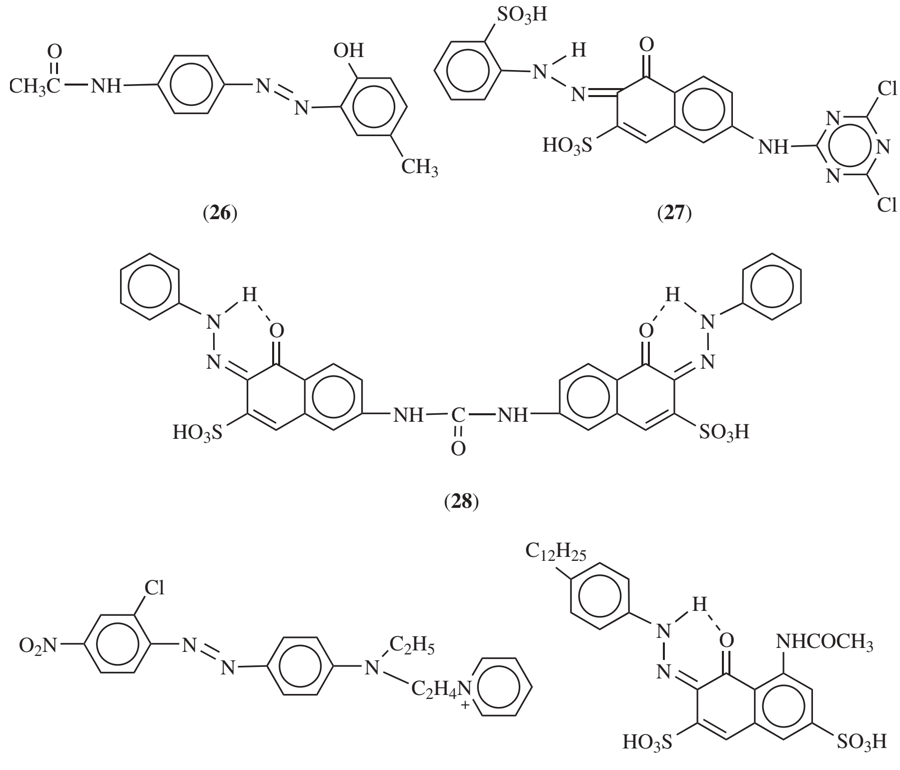
Metallization of dyes was originally carried out during the mordanting process to help fix the dye to the substrate. Premetallized dyes are now used widely in various outlets to improve the properties of the dye, particularly lightfastness. However, this is at the expense of brightness, since metallized azo dyes are duller than nonmetallized dyes.

Carbocyclic Azo Dyes. These dyes are the backbone of most commercial dye ranges. Based totally on benzene and naphthalene derivatives, they provide yellow, red, blue, and green colors for all the major substrates such as polyester, cellulose, nylon, polyacrylonitrile, and leather. Typical structures (**26–30**) are shown in Figure 4.

Most azoic dyes belong to the carbocyclic azo class, but these dyes are formed in the fiber pores during the application process.

The carbocyclic azo dye class provides dyes having high cost-effectiveness combined with good all-around fastness properties. However, they lack brightness, and consequently, they cannot compete with anthraquinone dyes for brightness. This shortcoming of carbocyclic azo dyes is overcome by heterocyclic azo dyes.

Heterocyclic Azo Dyes. One long-term aim of dyestuffs research has been to combine the brightness and high fastness properties of anthraquinone

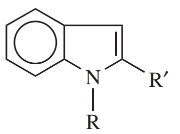


(26) (27) (28) (29) (30)

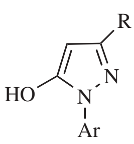
Fig. 4. Carbocyclic azo dyes. Disperse Yellow 3 [2832-40-8] (CI 11855) (**26**) is used to dye polyester; Reactive Orange 1 [6522-74-3] (CI 17907) (**27**) is a cotton dye; Direct Orange 26 [25188-23-2] (CI 29150) (**28**) is a dye for paper; Synacril Fast Red 2G [48222-26-0] (CI 11085) (**29**) dyes acrylic fibers; Acid Red 138 [93762-37-9] (CI 18073) (**30**) dyes nylon and wool.

dyes with the strength and economy of azo dyes. This aim is now being realized with heterocyclic azo dyes, which fall into two main groups: those derived from heterocyclic coupling components, and those derived from heterocyclic diazo components.

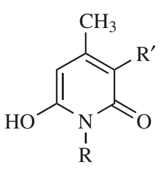
All the heterocyclic coupling components that provide commercially important azo dyes contain only nitrogen as the hetero atom. They are indoles (**31**), pyrazolones (**32**), and especially pyridones (**33**); they provide yellow to orange dyes for various substrates.



(31)



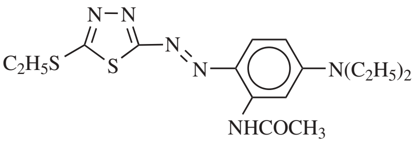
(32)



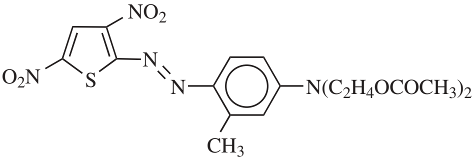
(33)

Many yellow dyes were of the azopyrazolone type, but nowadays, these have been largely superseded by azopyridone dyes. Azopyridone yellow dyes are brighter, stronger, and generally have better fastness properties than azopyrazolone dyes. They exist in the hydrazone tautomeric form.

In contrast to the heterocyclic coupling components, virtually all the heterocyclic diazo components that provide commercially important azo dyes contain sulfur, either alone or in combination with nitrogen (the one notable exception is the triazole system). These S or S/N heterocyclic azo dyes provide bright, strong shades that range from red through blue to green, and therefore complement the yellow–orange colors of the nitrogen heterocyclic azo dyes in providing a complete coverage of the entire shade gamut. Two representative dyes are the thiadiazole red [88779-75-3] (**34**) and a thiophene greenish blue (**35**). Both are disperse dyes for polyester, the second most important substrate after cellulose.



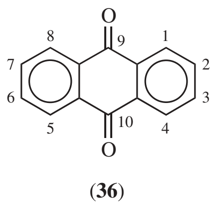
(**34**)



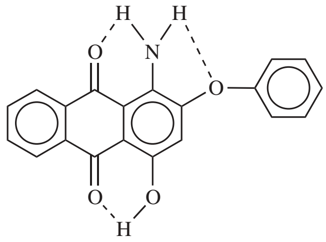
(**35**)

5.2. Anthraquinone Dyes. This second most important class of dyes also includes some of the oldest dyes; they have been found in the wrappings of mummies dating back over 4000 years. In contrast to the azo dyes, which have no natural counterparts, all the important natural red dyes were anthraquinones (see Dyes, natural). However, the importance of anthraquinone dyes is declining due to their low cost-effectiveness.

Anthraquinone dyes are based on 9,10-anthraquinone (**36**) [84-65-1] which is essentially colorless. To produce commercially useful dyes, powerful electron-donor groups such as amino or hydroxy are introduced into one or more of the four alpha positions (1,4,5, and 8). The most common substitution patterns are 1,4-, 1,2,4-, and 1,4,5,8-. To maximize the properties, primary and secondary amino groups (not tertiary) and hydroxy groups are employed. These ensure the maximum degree of π-orbital overlap, enhanced by intramolecular hydrogen bonding, with minimum steric hindrance. These features are illustrated in CI Disperse Red 60 [17418-58-5] (CI 60756) (**37**).



(**36**)



(**37**)

The strength of electron-donor groups increase in the order: $OH < NH_2 < NHR <$. Tetra-substituted anthraquinones (1,4,5,8-) are more bathochromic than di- (1,4-) or trisubstituted (1,2,4-) anthraquinones. Thus, by an appropriate selection of donor groups and substitution patterns, a wide variety of colors can be achieved (see Dyes, anthraquinone).

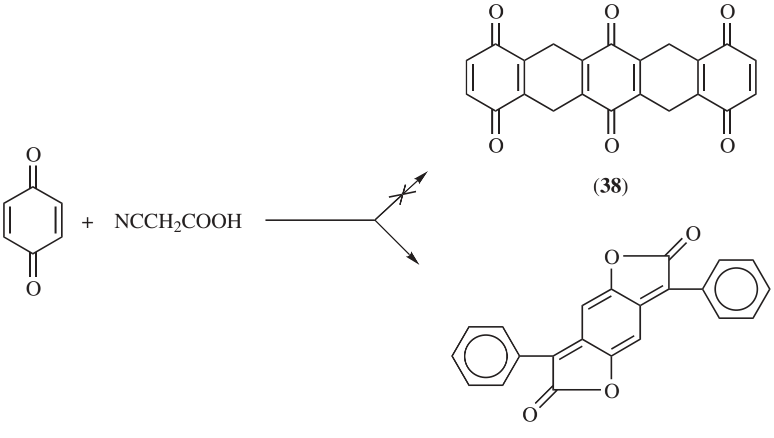
Synthesis. Anthraquinone dyes are prepared by the stepwise introduction of substituents onto the preformed anthraquinone skeleton (**36**) or ring closure of appropriately substituted precursors. The degree of freedom for producing a variety of different structures is restricted, and the availability of only eight substitution centers imposes a further restriction on synthetic flexibility. Therefore, there is significantly less synthetic flexibility than in the case of azo dyes, and consequently less variety; this is a drawback of anthraquinone dyes.

Tautomerism. Although tautomerism is theoretically possible in amino and hydroxy anthraquinone dyes, none has been observed. Studies by ^{13}C nmr have shown convincingly that amino and hydroxy dyes of 9,10-anthraquinone exist as such.

Metal Complexes. The main attributes of anthraquinone dyes are brightness and good fastness properties, including lightfastness. Metallization would detract from the former, and there is no need to improve the latter. Consequently, metallized anthraquinone dyes are of no importance.

Properties. The principal advantages of anthraquinone dyes are brightness and good fastness properties, but they are both expensive and tinctorially weak. However, they are still used extensively, particularly in the red and blue shade areas, because other dyes cannot provide the combination of properties offered by anthraquinone dyes, albeit at a price.

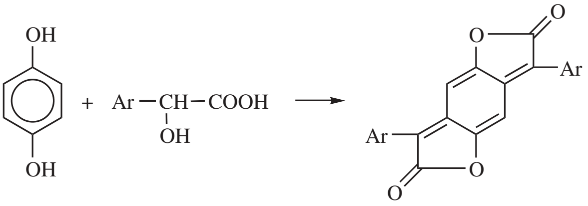
5.3. Benzodifuranone Dyes. These (BDF) dyes are challenging anthraquinone dyes. The BDF chromogen is one of the very few novel chromogens to have been discovered in this century. As with many other discoveries (10) the BDF chromogen was detected by accident. The pentacenequinone structure [100734-53-0] (**38**) assigned to the intensely red-colored product obtained from the reaction of *p*-benzoquinone with cyanoacetic acid was questioned (11). A compound such as (**38**) should not be intensely colored owing to the lack of conjugation. Instead, the red compound was correctly identified as the 3,7-diphenylbenzodifuranone [64501-49-1] (**39**) ($\lambda_{max} = 466$ nm; $\epsilon = 51,000$ in chloroform).

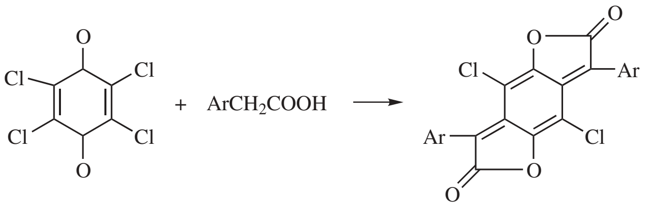


(**38**)

(**39**)

Improved syntheses from arylacetic acids and hydroquinone [123-31-9] or substituted quinones have been devised for BDF dyes (12).



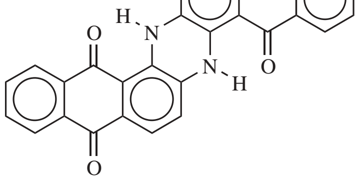


BDFs are unusual in that they span the whole color spectrum from yellow through red to blue, depending on the electron-donating power of the R group on the phenyl ring of the aryl acetic acid, ie, Ar = —C_6H_4R (R = H, yellow–orange; R = alkoxy, red; R = amion, blue). The first commercial BDF, Dispersol Red C-BN, a red disperse dye for polyester, is already making a tremendous impact. Its brightness even surpasses that of the anthraquinone reds, while its high tinctorial strength (ca 3–4 times that of anthraquinones) makes it cost-effective.

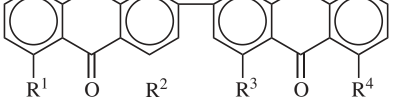
5.4. Polycyclic Aromatic Carbonyl Dyes.

Structurally, these dyes contain one or more carbonyl groups linked by a quinonoid system. They tend to be relatively large molecules built up from smaller units, typically anthraquinones. Since they are applied to the substrate (usually cellulose) by a vatting process, the polycyclic aromatic carbonyl dyes are often called the anthraquinonoid vat dyes.

Although the colors of the polycyclic aromatic carbonyl dyes cover the entire shade gamut, only the blue dyes and the tertiary shade dyes, namely, browns, greens, and blacks, are important commercially. Typical dyes are the blue indan throne [81-77-6] (**40**), the brown CI Vat Brown 3 [131-92-0] (CI 69012), (**41**), the black CI Vat Black 27 [2379-81-9] (**42**), and the green CI Vat Green 1 [128-58-5] (CI 59825) (**43**), probably the most famous of all the polycyclic aromatic carbonyl dyes.

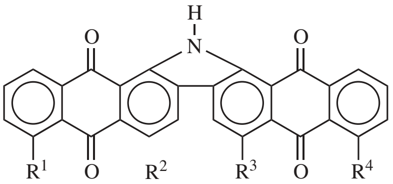


(**40**)



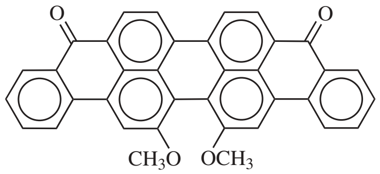
$R^1 = R^3 = C_6H_5CONH; R^2 = R^4 = H$

(**41**)



$R^1 = R^4 = H; R^2 = R^3 = C_6H_5CONH$

(**42**)

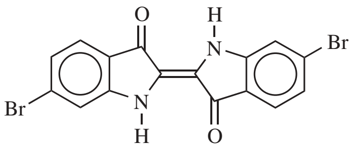


(**43**)

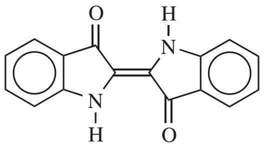
As a class, the polycyclic aromatic carbonyl dyes exhibit the highest order of lightfastness and wetfastness. The high lightfastness is undoubtedly associated with the absence of electron-donating and any further electron-withdrawing groups, other than carbonyl, thus restricting the number of photochemical sites in the molecule. The high wetfastness is a direct manifestation of the application process of the dyes.

5.5. Indigoid Dyes. Like the anthraquinone, benzodifuranone, and polycyclic aromatic carbonyl dyes, the indigoid dyes also contain carbonyl groups. They are also vat dyes.

Indigoid dyes represent one of the oldest known classes of dyes. For example, 6,6′-dibromoindigo [19201-53-7] (**44**) is Tyrian Purple, the dye made famous by the Romans. Tyrian Purple was so expensive that only the very wealthy were able to afford garments dyed with it. Indeed, the phrase “born to the purple” is still used today to denote wealth.



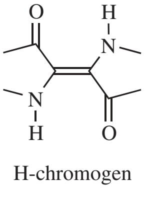
(**44**)



(**45**)

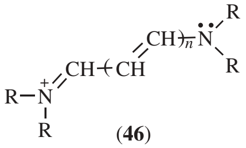
Although many indigoid dyes have been synthesized, only indigo [482-89-3] itself (**45**) is of any importance today. Indigo is the blue used almost exclusively for dyeing denim jeans and jackets and is held in high esteem because it fades in tone to give progressively paler blue shades.

One of the main fascinations of indigo is that such a small molecule should be blue. Normally, extensive conjugation, eg, phthalocyanines and/or several powerful donor and acceptor groups, eg, azo and anthraquinone dyes, are required to produce blue dyes. After much controversy it was proven that the chromogen, ie, that molecular species responsible for the color of indigo, is the crossed conjugated system (13–15). This surprising discovery prompted a new term for this kind of chromogen: it was called an H-chromogen because the basic shape resembled a capital H (16).



H-chromogen

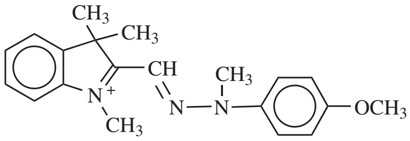
5.6. Polymethine and Related Dyes. Cyanine dyes (qv) (**46**) are the best known polymethine dyes. Nowadays, their commercial use is limited to sensitizing dyes for silver halide photography. However, derivatives of cyanine dyes provide important dyes for polyacrylonitrile.



where $n = 0, 1, 2, \ldots$ and R groups are typically part of ring systems

(**46**)

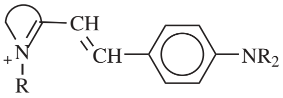
Azacarbocyanines. A cyanine containing three carbon atoms between heterocyclic nuclei is called a carbocyanine ($n = 1$ in (**46**)). Replacing these carbon atoms by one, two, and three nitrogen atoms produces azacarbocyanines, diazacarbocyanines, and triazacarbocyanines, respectively. Dyes of these three classes are important yellow dyes for polyacrylonitrile, eg, CI Basic Yellow 28 [52757-89-8] (CI 48054) (**47**).



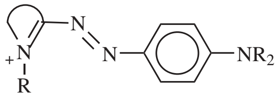
(**47**)

Hemicyanines. These half-cyanine dyes may be represented by structure (**48**). They may be considered as cyanines in which a benzene ring has been inserted into the conjugated chain. Hemicyanines provide some bright fluorescent red dyes for polyacrylonitrile.

Diazahemicyanines. Diazahemicyanine dyes are arguably the most important class of polymethine dyes. They have the general structure (**49**)

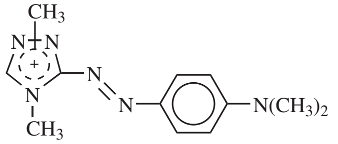


(**48**)

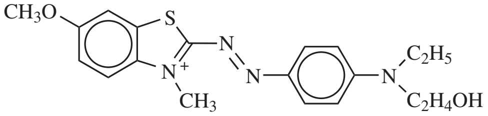


(**49**)

The heterocyclic ring is normally composed of one (eg, pyridinium), two (eg, pyrazolium and imidazolium), or three (eg, triazolium) nitrogen atoms, or sulfur and nitrogen atoms, eg, (benzo)thiazolium and thiadiazolium. Triazolium dyes (**50**) provide the market-leading red dyes for polyacrylonitrile, and a benzothiazolium dye (**51**) is the market-leading blue dye.

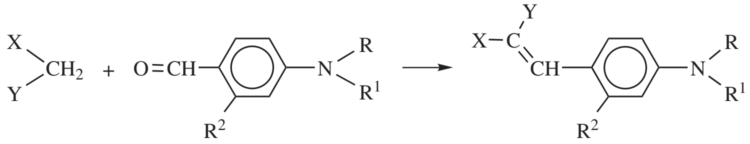


(**50**)



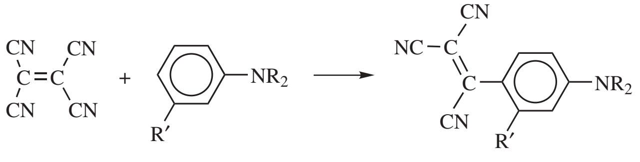
(**51**)

5.7. Styryl Dyes. The styryl dyes are uncharged molecules containing a styryl group $C_6H_5{-}CH{=}C$ usually in conjugation with an *N,N*-dialkylaminoaryl group. Styryl dyes were once a fairly important group of yellow dyes for a variety of substrates. They are synthesized by condensation of an active methylene compound, especially malononitrile [109-77-3] (**52**); X = Y = CN with a carbonyl group, especially an aldehyde. As such, styryl dyes have small molecular structures and are ideal for dyeing densely packed hydrophobic substrates such as polyester. CI Disperse Yellow 31 [4361-84-6] (**53**), $R = C_4H_9$, $R^1 = C_2H_4Cl$, $R^2 = H$, X = CN, $Y = COOC_2H_5$, is a typical dye.

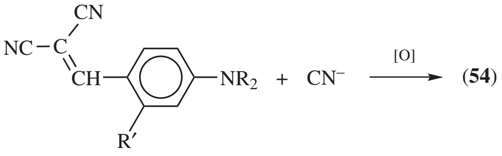


(**52**) (**53**)

Yellow styryl dyes have now been largely superseded by superior dyes such as azopyridones, but there has been a resurgence of interest in red and blue styryl dyes. The addition of a third cyano group to produce a tricyanovinyl group causes a large bathochromic shift: the resulting dyes, eg, (**54**), are bright red rather than the greenish yellow color of the dicyanovinyl dyes. These tricyanovinyl dyes have been patented by Mitsubishi for the transfer printing of polyester substrates. Two synthetic routes to the dyes are shown: one is by the replacement of a cyano group in tetracyanoethylene, and the second is by oxidative cyanation of a dicyanovinyl dye (**55**) with cyanide. The use of such toxic reagents could hinder the commercialization of the tricyanovinyl dyes (see CYANOCARBONS).

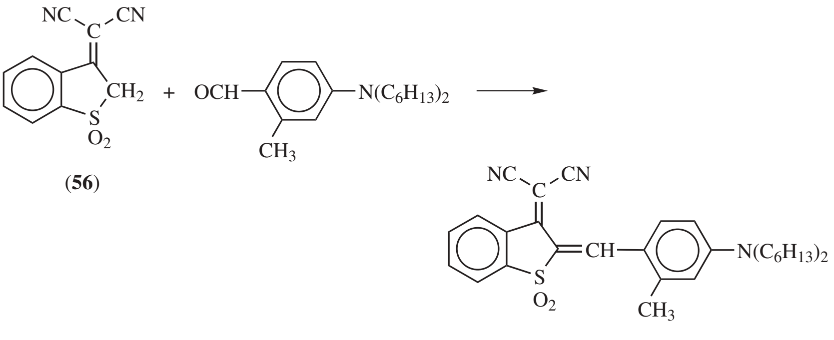


(**54**)



(**55**)

Blue styryl dyes are produced when an even more powerful electron-withdrawing group than tricyanovinyl is used. Thus, Sandoz discovered that the condensation of the sulfone (**56**) [74228-25-4] with an aldehyde gives the bright blue dye (**57**) for polyester. In addition to exceptional brightness, this dye also possesses high tinctorial strength ($\epsilon_{\max} \sim 70,000$). However, its lightfastness is only moderate.



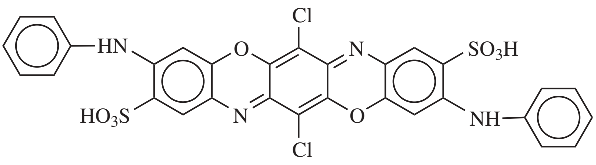
(**56**)

(**57**)

5.8. Di- and Triaryl Carbonium and Related Dyes. The structural interrelationships of the diarylcarbonium dyes (**58**), triarylcarbonium dyes (**59**), and their heterocyclic derivatives are shown in Figure 5. As a class, the dyes are bright and strong, but are generally deficient in lightfastness. Consequently, they are used in outlets where brightness and cost-effectiveness, rather than permanence, are paramount, for example, the coloration of paper. Many dyes of this class, especially derivatives of pyronines (xanthenes), are among the most fluorescent dyes known.

Typical dyes are the diphenylmethane, Auramine O ((**60**); $R = CH_3$, $X = C{-}NH_2$; CI Basic Yellow 2) [2465-27-2]; the triphenylmethane, Malachite Green ((**59**) $R = CH_3$; $R' = H$; CI Basic Green 4) [569-64-2]; the thiazine dye Methylene Blue ((**62**); $R = CH_3$; CI Basic Blue 9) [61-73-1] (CI 52015) used extensively in the Gram staining test for bacteria; the oxazine dye, CI Basic Blue 3 ((**63**); $R = C_2H_5$) [47367-75-9]; and the xanthene dye, CI Acid Red 52 (**64**) [121313-93-7].

Notable advances have been made in recent years in triphendioxazine dyes (see AZINE DYES). Triphendioxazine direct dyes have been known for many years; CI Direct Blue 106 (**65**) is a typical dye. Resurgence of interest in triphendioxazine dyes arose through successful modification of the intrinsically strong and bright triphendioxazine chromogen to produce blue reactive dyes for cotton (17). These blue reactive dyes combine the advantages of azo dyes and anthraquinone dyes. Thus they are bright, strong dyes with good fastness properties. Structure (**66**) is typical of these reactive dyes. R represents the reactive group.



(**65**)

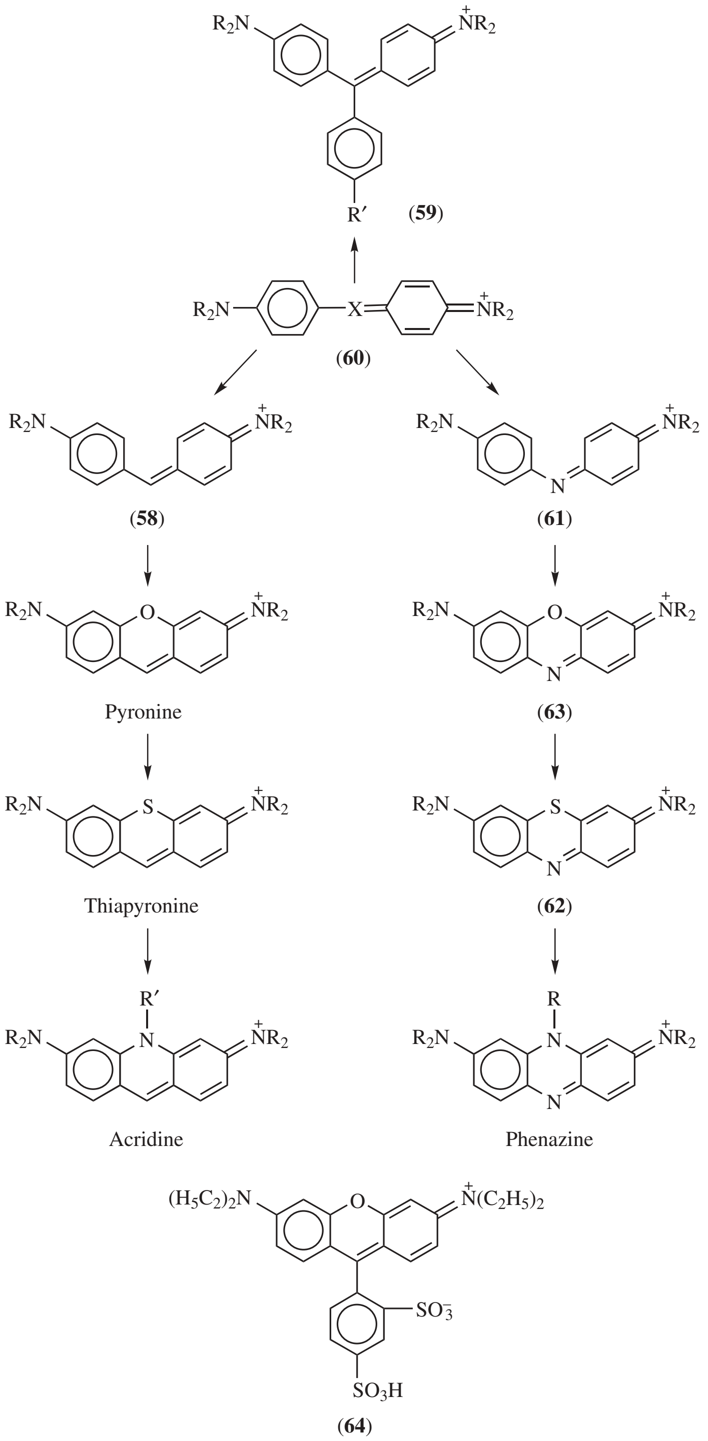
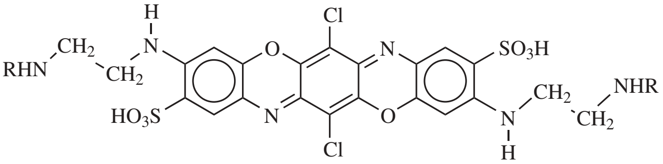


Fig. 5. Structural interrelationships among diaryl and triaryl carbonium dyes. Pyronine = xanthene; (**61**), R = CH_3 is Bindschedler's Green.

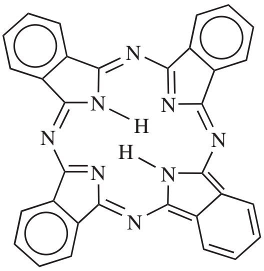


(**66**)

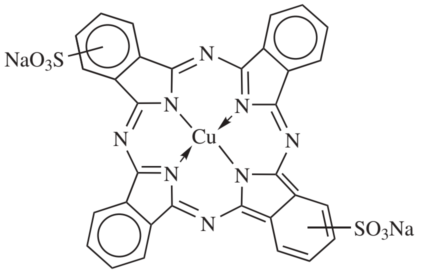
Like phthalocyanine dyes, triphendioxazine dyes are large molecules, and therefore their use is restricted to coloring the more open-structured substrates such as paper and cotton.

5.9. Phthalocyanines. Phthalocyanine is the only novel chromogen of commercial importance discovered since the nineteenth century. It was discovered accidently in 1928, when during the routine manufacture of phthalimide from phthalic anhydride and ammonia it was found that the product contained a blue contaminant. Chemists of Scottish Dyes Ltd, now part of Zeneca, carried out an independent synthesis of the blue material by passing ammonia gas into molten phthalic anhydride containing iron filings. The importance of the colorant was realized (it was intensely colored and very stable), and a patent application was filed in the same year.

The structure of the blue material was not elucidated until 1934, when it was shown to be the iron complex of (**67**). The new material was christened phthalocyanine [574-93-6], reflecting both its origin from phthalic anhydride and its beautiful blue color (like cyanine dyes). A year later the structure was confirmed by one of the first uses of x-ray crystallography.



(**67**)



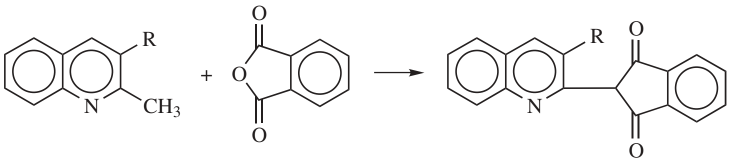
(**68**)

Phthalocyanines are analogues of the natural pigments chlorophyll and heme. However, unlike these natural pigments, which have extremely poor stability, phthalocyanines are probably the most stable of all the colorants in use today. Substituents can extend the absorption to longer wavelengths, into the near infrared, but not to shorter wavelengths, and so their hues are restricted to blue and green.

Of all the metal complexes evaluated, copper phthalocyanines give the best combination of color and properties and consequently the majority of phthalocyanine dyes are based on copper phthalocyanine; CI Direct Blue 86 [1330-38-7] (CI 74180) (**68**) is a typical dye.

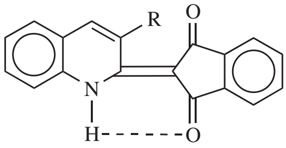
As well as being extremely stable, phthalocyanines are bright and tinctorially strong ($\epsilon_{\max} \sim 100,000$); this renders them cost-effective. Consequently, phthalocyanines are used extensively in printing inks and paints. The preponderance of blue and green labeling on products is testament to the popularity of phthalocyanine-based printing inks, and most blue and green cars are the product of phthalocyanine-based paints (see PHTHALOCYANINE COMPOUNDS).

5.10. Quinophthalones. Like the hydroxy azo dyes, quinophthalone dyes can, in theory, exhibit tautomerism. Because the dyes are synthesized by the condensation of quinaldine derivatives (**69**) with phthalic anhydride, they are often depicted as structure (**70**), but this is incorrect, since the two single bonds prevent any conjugation between the two halves of the molecule.



(**69**) (**70**)

The dyes exist as structure (**71**),

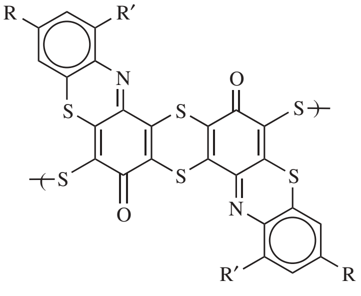


(**71**)

in which the donor pyrrole-type nitrogen atom is conjugated to the two acceptor carbonyl groups via an ethylenic bridge. In addition to the increased conjugation, structure (**71**) is stabilized further by the six-membered intramolecular hydrogen bond between the imino hydrogen atom and the carbonyl oxygen atom.

Quinophthalones provide important dyes for the coloration of plastics (eg, CI Solvent Yellow 33 (**71**), R = H [5662-03-3]) and for the coloration of polyester. For example, CI Disperse Yellow 54 (**71**) R = OH, is the leading yellow dye for the transfer printing of polyester.

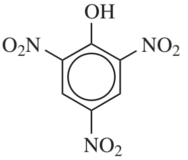
5.11. Sulfur Dyes. These dyes are synthesized by heating aromatic amines, phenols, or nitro compounds with sulfur or, more usually, alkali polysulfides. Unlike most other dye types, it is not easy to define a chromogen for the sulfur dyes (qv). It is likely that they consist of macromolecular structures of the phenothiazone-thianthrone type (**72**), in which the sulfur is present as (sulfide) bridging links and thiazine groups (1).



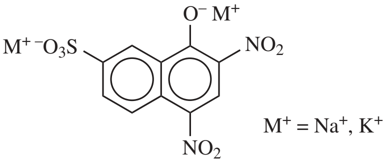
(**72**)

Sulfur dyes are used for dyeing cellulosic fibers. They are insoluble in water and are reduced to the water-soluble leuco form for application to the substrate by using sodium sulfide solution. The sulfur dye proper is then formed within the fiber pores by atmospheric oxidation (5). Sulfur dyes constitute an important class of dye for producing cost-effective tertiary shades, especially black, on cellulosic fibers. One of the most important dyes is CI Sulfur Black 1 [1326-82-5] (CI 53185), prepared by heating 2,4-dinitrophenol with sodium polysulfide.

5.12. Nitro and Nitroso Dyes. These dyes are now of only minor commercial importance, but are of interest for their small molecular structures. The early nitro dyes were acid dyes used for dyeing the natural animal fibers such as wool and silk. They were nitro derivatives of phenols, eg, picric acid [88-89-1] (**73**) (CI 10305), or naphthols, eg, CI Acid Yellow 1 [846-70-8] (**74**) (CI 10316).

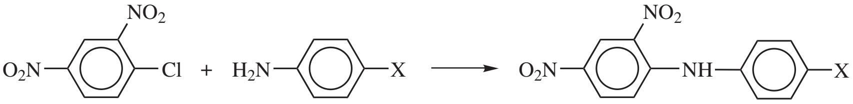


(**73**)



(**74**)

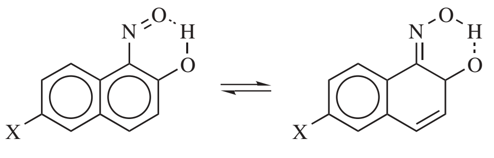
The most important nitro dyes are the nitrodiphenylamines of general structure (**75**).



(**75**)

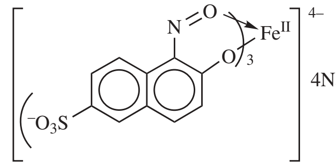
These small molecules are ideal for penetrating dense fibers such as polyester, and are therefore used as disperse dyes for polyester. All the important dyes are yellow: in (**75**) X = H is CI Disperse Yellow 14 [961-68-2]; X = OH is CI Disperse Yellow 1 [119-15-3]; and X = NH_2 is CI Disperse Yellow 9 [6373-73-5]. Although the dyes are not terribly strong ($\epsilon_{\max} \sim 20,000$), they are cost-effective because of their easy synthesis from inexpensive intermediates. CI Disperse Yellow 42 [5124-25-4] and CI Disperse Yellow 86 are important lightfast dyes for automotive-grade polyester.

Nitroso dyes are metal-complex derivatives of *o*-nitrosophenols or naphthols. Tautomerism is possible in the metal-free precursor between the nitrosohydroxy tautomer (**76**) and the quinoneoxime tautomer (**77**).



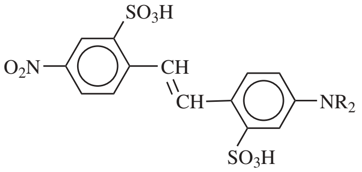
(**76**) (**77**)

The only nitroso dyes important commercially are the iron complexes of sulfonated 1-nitroso-2-naphthol, eg, CI Acid Green 1 [57813-94-2] (**78**) (CI 10020); these inexpensive colorants are used mainly for coloring paper.

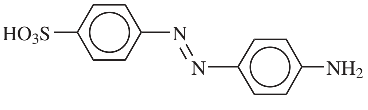


(**78**)

5.13. Miscellaneous Dyes. Other classes of dyes that still have some importance are the stilbene dyes and the formazan dyes. *Stilbene dyes* are in most cases mixtures of dyes of indeterminate constitution that are formed from the condensation of sulfonated nitroaromatic compounds in aqueous caustic alkali either alone or with other aromatic compounds, typically arylamines (5). The sulfonated nitrostilbene [128-42-7] (**79**) is the most important nitroaromatic, and the aminoazobenzenes are the most important arylamines. CI Direct Orange 34 [2222-37-6] (CI 40215-40220), the condensation product(s) of (**79**) and the aminoazobenzene [104-23-4] (**80**), is a typical stilbene dye.

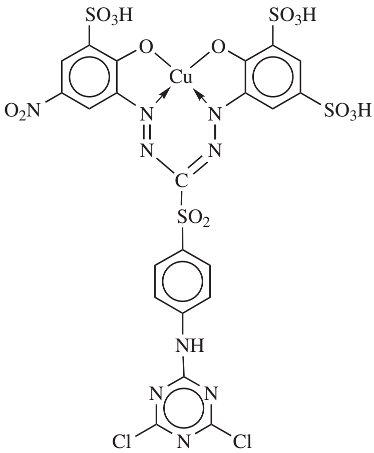


(**79**)



(**80**)

Formazan dyes bear a formal resemblance to azo dyes, since they contain an azo group but have sufficient structural dissimilarities to be considered as a separate class of dyes. The most important formazan dyes are the metal complexes, particularly copper complexes, of tetradentate formazans. They are used as reactive dyes for cotton; (**81**) is a representative example.



(**81**)

6. Dye Intermediates

The precursors of dyes are called dye intermediates. They are obtained from simple raw materials, such as benzene and naphthalene, by a variety of chemical reactions. Usually, the raw materials are cyclic aromatic compounds, but acyclic precursors are used to synthesize heterocyclic intermediates. The intermediates are derived from two principal sources, coal tar and petroleum (qv).

6.1. Sources of Raw Materials. Coal tar results from the pyrolysis of coal (qv) and is obtained chiefly as a by-product in the manufacture of coke for the steel industry (see COAL, CARBONIZATION). Products recovered from the fractional distillation of coal tar have been the traditional organic raw material for the dye industry. Among the most important are benzene (qv), toluene (qv), xylene naphthalene (qv), anthracene, acenaphthene, pyrene, pyridine (qv), carbazole, phenol (qv), and cresol (see also ALKYLPHENOLS; ANTHRAQUINONE; XYLENES AND ETHYLBENZENES).

The petroleum industry is now the principal supplier of benzene, toluene, the xylenes, and naphthalene (see BTX PROCESSING; FEEDSTOCKS). Petroleum displaced coal tar as the primary source for these aromatic compounds after World War II because it was relatively cheap and abundantly available. However, the re-emergence of king coal is predicted for the twenty-first century, when oil supplies are expected to dwindle and the cost of producing chemicals from coal (including new processes based on synthesis gas) will gradually become more competitive (3).

6.2. Intermediates Classification. Intermediates may be conveniently divided into primary intermediates (primaries) and dye intermediates. Large amounts of inorganic materials are consumed in both intermediates and dyes manufacture.

Inorganic Materials. These include acids (sulfuric, nitric, hydrochloric, and phosphoric), bases (caustic soda, caustic potash, soda ash, sodium carbonate, ammonia, and lime), salts (sodium chloride, sodium nitrite, and sodium sulfide) and other substances such as chlorine, bromine, phosphorus chlorides, and sulfur chlorides. The important point is that there is a significant usage of at least one inorganic material in all processes, and the overall tonnage used by, and therefore the cost to, the dye industry is high.

Primary Intermediates. Primary intermediates are characterized by one or more of the following descriptions, which associate them with raw materials rather than with intermediates.

1. Manufactured in a dedicated plant, ie, one devoted to a single product or at most two or three closely related products.
2. At least 1000 t/yr capacity from a single plant and may be up to 100,000 t/yr, eg, aniline.
3. Manufacturing process and/or operation is continuous or semicontinuous, ie, at least one stage is in a continuous, as distinct from batch, mode.
4. A primary intermediate has established usage in basic industries such as rubber, polymers, or agrochemicals in addition to dyes.

Primary intermediates were originally manufactured within the dyes industry. All the significant primaries, about 30 different products, are derived from benzene, toluene, or naphthalene. Actual production figures for primaries are not readily available, and in any event the amounts used within the dyes industry are variable. The primaries are listed here with a reference to the *Encyclopedia* article that covers them in detail including production and consumption figures.

The following amines are covered under the title AMINES, AROMATIC:

aniline	dimethylaniline
p-nitroaniline	*m*-phenylenediamine
o-toluidine	*p*-phenylenediamine
p-toluidine	

The article NITROBENZENES AND NITROTOLUENES covers the primaries:

nitrobenzene	*o*-chloronitrotoluene
p-chloronitrobenzene	*p*-nitrotoluene

Some primaries have articles devoted to them and their derivatives, ie, BENZOIC ACID, PHENOL, SALICYLIC ACID, and PHTHALIC ANHYDRIDE as a derivative of phthalic acid. The primary β-naphthol is discussed in NAPHTHALENE DERIVATIVES.

Dye Intermediates. Dye intermediates are defined as those precursors to colorants that are manufactured within the dyes industry, and they are nearly always colorless. Colored precursors are conveniently termed color bases. As distinct from primaries they are only rarely manufactured in single-product units because of the comparatively low tonnages required. Fluorescent brightening agents (FBAs) are neither intermediates nor true colorants. Basic manufacturing processes for FBAs are described in Reference 18 (see FLUORESCENT WHITENING AGENTS).

There are at least 3000 different intermediates in current manufacture (over half that number are specifically mentioned in the *Colour Index*), and in addition there is a comparatively small number of products manufactured by individual companies for their own specialties. Only a selection of intermediates can be discussed here, but since 300 of the products probably account for 90% of the quantity of intermediates used, most of the important aspects can be covered. No meaningful quantification of world tonnage requirements of primaries and intermediates for dyes can be made.

Intermediates vary in complexity, usually related to the number of chemical and operational stages in their manufacture, and therefore cost. Prices may be classed as cheap (less than \$1500/t, as with primaries), average (\$1500 to \$5000/t) or expensive (more than \$5000/t).

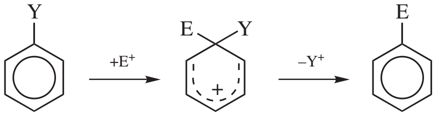
7. The Chemistry of Dye Intermediates

The chemistry of dye intermediates may be conveniently divided into the chemistry of carbocycles, such as benzene and naphthalene, and the chemistry of heterocycles, such as pyridones and thiophenes.

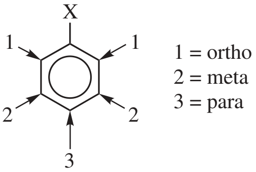
7.1. Chemistry of Aromatic Carbocycles.

Benzene and naphthalene are by far the most important aromatic carbocycles used in the dyes industry. The hundreds of benzene and naphthalene intermediates used can be prepared from these parent compounds by the sequential introduction of a variety of substituents eg, NO_2, NR^1R^2, Cl, SO_3H, etc. Introduction of these groups are known as unit processes. The substituents are introduced into the aromatic ring by either electrophilic or nucleophilic substitution. In general, aromatic rings, because of their inherently high electron density, are much more susceptible to electrophilic attack than to nucleophilic attack. Nucleophilic attack only occurs under forcing conditions unless the aromatic ring already contains a powerful electron-withdrawing group, eg, NO_2. In this case, nucleophilic attack is greatly facilitated because of the reduced electron density at the ring carbon atoms.

Electrophilic Substitution. The most common mechanism for electrophilic attack at an aromatic system involves the initial attack of an electrophile E^+ to give an intermediate containing a tetrahedral carbon atom; loss of Y^+, usually a proton, from the intermediate, then gives the product:



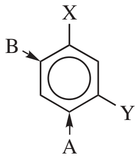
Attack of an unsubstituted benzene ring can lead to only one monosubstitution product. However, when electrophilic attack occurs at a benzene ring already containing a group, there are three possible sites of attack.



Fortunately, the position of attack may be predicted with a fair degree of accuracy because the various X groups are known to fall into two main categories: those directing the incoming electrophile to the ortho and para positions, and those directing it to the meta position (19) (see BENZENE). The directing effect of the substituent is not exclusive, but is usually sufficient to give one type of product. Thus nitration of nitrobenzene gives approximately 93% of meta, 6% of ortho, and 1% of para dinitrobenzene.

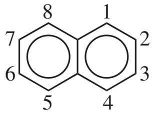
The majority of ortho-para directing groups are also activating substituents (with respect to hydrogen) whereas meta directing substituents are deactivating. The halogens, F, Cl, Br, and I, are peculiar in that they deactivate the benzene ring to electrophilic attack, yet direct the incoming substituent to the ortho and para positions.

When the benzene ring contains more than one group it is usually harder to predict where the incoming substituent will enter. However, a few simple rules have been formulated for disubstituted benzene rings: (*1*) if the two groups favor attack at one position, then the electrophile will attack there; (*2*) if a strongly activating group competes with a group that deactivates or only weakly activates the benzene ring, then the position of attack is controlled by the strongly activating group; (*3*) for steric reasons, an electrophile is least likely to attack the position between two groups in a meta aspect to each other; (*4*) in the situation shown by the following, attack will take place at position A rather than B.



X electron donor (*o*, *p*-director)
Y electron acceptor (*m*-director)

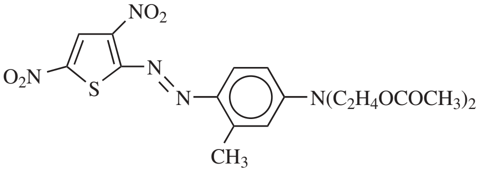
The other important carbocyclic ring system used in dyes is naphthalene [91-20-3]. Here the preferred position of attack is the 1-position. However, 2-substituted naphthalenes are thermodynamically more stable, and under equilibrating conditions the 2-isomer is formed in preference to the 1-isomer.



Activating substituents in one of the rings of naphthalene promote substitution in that ring. Deactivating substituents deactivate the ring to which they are attached and electrophilic substitution occurs in the other ring. These effects may be explained by similar arguments to those for benzene substitution patterns and many analogies may be drawn between the two systems.

Nucleophilic Substitution. The unsubstituted benzene ring is not susceptible to nucleophilic attack. However, if the benzene ring contains a good leaving group, eg, Cl, and a strong electron-withdrawing substituent, eg, NO_2, in an ortho and para position, then nucleophilic substitution is greatly facilitated.

The most important mechanism for nucleophilic aromatic substitution is the S_NAr mechanism. The first step is usually rate determining since this is the step in which the aromaticity is lost.



(**35**)

The S_N1 mechanism, in which the substituent leaves before the incoming nucleophile attacks, is less frequently encountered, although it is known to occur in the substitution of the diazonium group

$$(\text{—}\overset{+}{N}\equiv N).$$

Orientation in nucleophilic aromatic substitution is not problematic since the nucleophile usually replaces the leaving group, although there are exceptions, eg, those involving benzyne intermediates. As in nucleophilic aliphatic substitution, the common leaving groups are the halides, sulfonates, and ammonium salts. In addition, nitro, alkoxy, sulfone, and sulfonic acid groups are frequently encountered as leaving groups in aromatic substitution (20).

Unit Processes. The unit processes encountered in intermediate and dye chemistry are summarized in Table 2.

Nitration. The unit process of nitration (qv) is concerned with the introduction of one or more nitro (NO_2) groups into an aromatic nucleus by the replacement of a hydrogen atom. For the more important intermediates, the reaction is achieved by the addition of nitric acid, usually in combination with sulfuric acid (mixed acid), to a sulfuric acid solution of the reactant. The nitronium ion ($NO^{+}{}_{2}$) is the active nitrating species, and the key process variables that affect yield and quality of product are concentration, temperature, and mixed acid composition. The nitro product is obtained by drowning out (ie, adding to excess water with internal or external cooling as required) followed by separation or extraction.

The largest scale nitrations are typically those in which the nitro compounds are precursors of amine primaries. When nitrating benzene, toluene, chlorobenzene, and naphthalene, continuous operation in custom-built plants

Table 2. **Unit Processes in Dyes Manufacture**

Process	Primaries[a]	Intermediates (common usage)	Colorants (common usage)
nitration	6	✓	
reduction	8	✓	
sulfonation	4	✓[b]	✓
oxidation	5	✓	
fusion/hydroxylation	3	✓	
amination	3	✓[c]	
alkylation	2	✓	✓
halogenation	2	✓	✓
hydrolysis	2	✓	
condensation	1	✓	✓
alkoxylation	1	✓	
esterification	1	✓	
carboxylation	1	✓	
acylation	1	✓	✓
phosgenation	1	✓	✓
diazotization	1	✓	✓
coupling (azo)	1	✓	✓

[a] Number of occurrences within 30 identified product manufactures.

[b] Includes chlorosulfonation.

[c] Includes the Bucherer reaction.

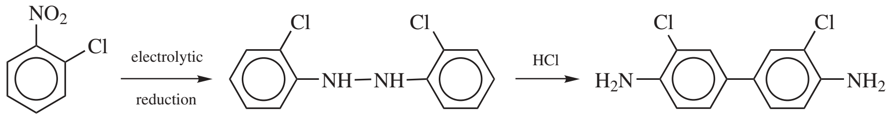
can normally be justified. These primary nitro products are also typical of the isomer patterns and separation processes that are encountered in more highly substituted molecules. Apart from the normal economic advantages of continuous operation, continuous nitration offers better controlled conditions, which together with a lower in-process inventory, lead to safer operation. The remaining smaller scale nitrations are typically carried out in multiproduct nitration units. Occasionally nitration is combined with sulfonation to give a telescoped two-stage reaction in a single unit.

The reaction vessel (nitrator) is constructed of cast iron, mild carbon steel, stainless steel, or glass-lined steel depending on the reaction environment. It is designed to maintain the required operating temperature with heat-removal capability to cope with this strongly exothermic and potentially hazardous reaction. Secondary problems are the containment of nitric oxide fumes and disposal or reuse of the dilute spent acid. Examples of important intermediates resulting from nitration are summarized in Table 3.

Reduction. The most important reduction process is the conversion of an aromatic nitro or dinitro compound into an arylamine or arylene diamine. The six hydrogen atoms per nitro group that are required ($RNO_2 + 6H \longrightarrow RNH_2 + 2H_2O$) are provided either directly, by catalytic hydrogenation, or indirectly, using a wide range of reagents and operating conditions.

The industrial processes used for reduction are catalytic hydrogenation, iron reduction (aqueous neutral or acidic, or solvent), and sulfide reduction. Sulfide is used for the selective reduction of dinitro compounds to nitroarylamines, and for metal-sensitive systems, such as certain substituted 2-aminophenols. It is also used to selectively reduce nitro groups, and not the azo groups, in nitroazo dyes. These are illustrated in Table 4.

Benzidine chemistry involves reduction. The nitro precursor is reduced either by zinc and alkali or electrolytically to the hydrazo intermediate, which is then transformed to the benzidine by treatment with acid.



Although manufacture of benzidine itself has virtually ceased in Europe and the United States, similar rearrangement processes are operated for 3,3′-dichlorobenzidine [91-94-1], *o*-dianisidine (3,3′-dimethoxybenzidine), and benzidine-2,2′-disulfonic acid.

Another important reduction process is that of aryldiazonium salts with sulfite/bisulfite at controlled pH to produce arylhydrazines. Arylhydrazines are important intermediates for the preparation of pyrazolones and indoles.

In the benzene and naphthalene series there are few examples of quinone reductions other than that of hydroquinone itself. There are, however, many intermediate reaction sequences in the anthraquinone series that depend on the generation, usually by employing aqueous “hydros” (sodium dithionite) of the so-called leuco compound. The reaction with leuco quinizarin [122308-59-2]

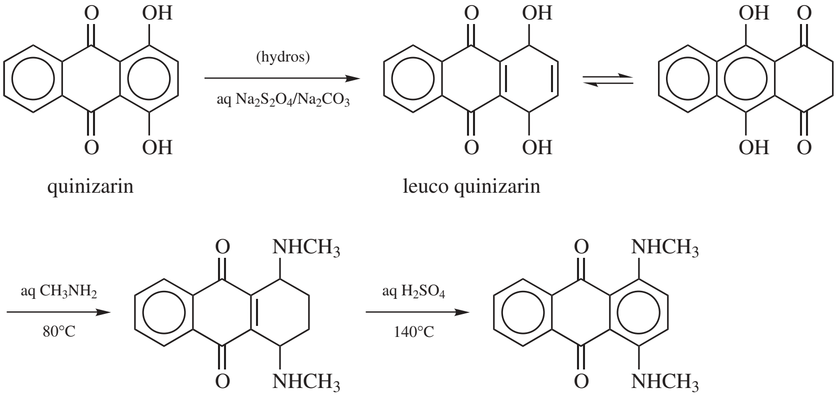
Table 3. **Dye Intermediates Obtained by Nitration**

Product	CAS Registry number	Starting material	Nitration process
1,2,-dichloro-4-nitro-benzene	[99-54-7]	*o*-dichlorobenzene	mixed acid/30°C and purification from isomers
1,4-dichloro-2-nitro-benzene	[89-61-2]	*p*-dichlorobenzene	mixed acid/30°C
1,8-dinitronaphthalene	[602-38-0]	naphthalene	mixed acid/80°C (50% yield 1,8 + 25% 1,5 after separation)
1,5-dinitronaphthalene	[605-71-0]		
8-nitronaphthalene-1-sulfonic acid	[112-41-9]	naphthalene-1-sulfonic acid	HNO_3/30°C
5-nitronaphthalene-1-sulfonic acid	[17521-00-5]		
3-nitronaphthalene-1,5-disulfonic acid	[117-86-2]	naphthalene-1,5-disulfonic acid	HNO_3/oleum to minimize 4-nitro
1-nitronaphthalene-3,6,8-trisulfonic acid	[38267-31-1]	naphthalene-1,3,6-trisulfonic acid	mixed acid/40°C through process
6-nitrodiazo-1,2,4-acid		diazo-1,2,4-acid	mixed acid/5°C (95% yield)
1-nitroanthraquinone	[82-34-8]	anthraquinone	HNO_3/85% sulfuric acid
1,8-dinitroanthraqui-none	[129-39-5]	1-nitroanthra-quinone	HNO_3/monohydrate/100°C separation by fractional crystallization
1,5-dinitroanthraqui-none	[82-35-9]		
4,8-dinitroanthrarufin-2,6-disulfonic acid	[6449-09-8]	anthrarufin (1,5-dihydroxy-anthraquinone)	oleum sulfonation followed by mixed acid/30°C
4,5-dinitrochrysazin (plus an isomeric byproduct)	[81-55-0]	chrysazin (1,8-dihydroxy-anthraquinone)	HNO_3/oleum/0°C
2-amino-5-nitrophenol	[121-88-0]	2-methylbenz-oxazolone (protected form of 2-aminophenol)	mixed acid/0−10°C followed by hydrolysis and separation from 4-nitro isomer
2-amino-5-nitrothiazole	[121-66-4]	2-aminothiazole nitrate	low temperature rearrangement

Table 4. **Arylamine Dye Intermediates Obtained by Reduction**

Product	CAS Registry number	Starting material	Reduction process
aniline	[62-53-3]	nitrobenzene	catalytic hydrogenation
m-phenylenediamine	[108-45-7]	*m*-dinitrobenzene	catalytic hydrogenation
m-nitroaniline		*m*-dinitrobenzene	sulfide
p-chloroaniline	[95-51-2]	*p*-chloronitro-benzene	iron
2,5-dichloroaniline	[95-82-9]	2-nitro-1,4-dichlorobenzene	iron
m-toluidine	[108-44-1]	*m*-nitrotoluene	iron or catalytic hydrogenation
p-toluidine	[106-49-0]	*p*-nitrotoluene	catalytic hydrogenation
1-naphthylamine	[134-32-7]	1-nitronaphthalene	catalytic hydrogenation
o-aminophenol	[95-55-6]	*o*-nitrophenol	sulfide
2-amino-4-nitro-phenol	[99-57-0]	2,4-dinitrophenol	sulfide/ammonia
2-amino-4-chloro-phenol	[95-85-2]	4-chloro-2-nitrophenol	iron/H_2SO_4
2-amino-6-chloro-4-nitrophenol	[6358-09-4]	6-chloro-2,4-dinitrophenol	sulfide
o-anisidine	[90-04-0]	*o*-nitroanisole	iron/formic acid
orthanilic acid	[88-21-1]	*o*-nitrobenzene-sulfonic acid	iron
metanilic acid	[121-47-1]	*m*-nitrobenzene-sulfonic acid	iron or catalytic hydrogenation
Laurent's acid	[84-89-9]	1-nitronaphthalene-5-sulfonic acid	iron; may be separated after reduction of mixed nitro isomers
peri acid	[82-75-7]	1-nitronaphthalene-8-sulfonic acid	
2-naphthylamine-4,8-disulfonic acid	[131-27-1]	3-nitronaphthalene-1,5-disulfonic acid	iron
Koch acid	[117-42-0]	8-nitronaphthalene-1,3,6-trisulfonic acid	iron
1,6-Cleves acid	[119-79-9]	5/8-nitronaph-thalene-2-sulfonic acid	iron
1,7-Cleves acid	[119-28-8]		
2-aminophenol-4-sulfonic acid	[98-37-3]	2-nitrophenol-4-sulfonic acid	sulfide
6-nitro-2-aminophenol-4-sulfonic acid	[96-93-5]	2,6-dinitrophenol-4-sulfonic acid	sulfide
p-phenylenediamine	[106-50-3]	*p*-nitroaniline	iron (90% yield) or catalytic hydrogenation
p-aminoacetanilide	[122-80-5]	*p*-nitroacetanilide	iron
p-phenylenediamine-sulfonic acid	[88-45-9]	4-nitroaniline-2-sulfonic acid	iron
4,4′-diaminostilbene-2,2′-disulfonic acid	[81-11-8]	4,4′-dinitrostilbene-2,2′-disulfonic acid	iron
1-aminoanthraqui-none		1-nitroanthra-quinone	sulfide
1,5-diaminoanthra-quinone	[129-44-2]	1,5-dinitro-anthraquinone	sulfide or NH_3 amination
1,8-diaminoanthra-quinone	[129-42-0]	1,8-dinitro-anthraquinone	
4,5-diaminochrysazin (crude)	[128-94-9]	4,5-dinitro-chrysazin	sulfide
4,8-diaminoanthra-rufin-2,6-disulfonic acid	[128-86-9]	4,8-dinitroanthra-rufin-2,6-disulfonic acid	sulfide

is shown because this provides the key route to the important 1,4-diaminoanthraquinones.



quinizarin

leuco quinizarin

1,4-bis(methylamino)anthraquinone

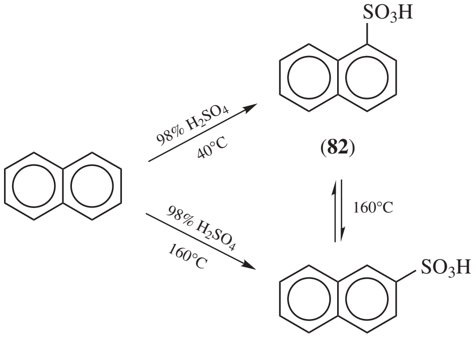
Arylalkylsulfones are important intermediates obtained by alkylation of arylsulfinic acids. The latter are obtained by reduction of the corresponding sulfonyl chloride. This reduction process is simple and of general application involving the addition of the isolated sulfonyl chloride paste to excess aqueous sodium sulfite followed by salting-out the product and isolation. With more rigorous reduction conditions, such as zinc/acid, sulfonyl chlorides are reduced through to arylmercaptans, eg, 2-mercaptonaphthalene is manufactured from naphthalene-2-sulfonyl chloride.

Sulfonation. The sulfonic acid group is used extensively in the dyes industry for its water-solubilizing properties, and for its ability to act as a good leaving group in nucleophilic substitutions. It is used almost exclusively for these purposes since it has only a minor effect on the color of a dye.

The sulfonic acid group can be introduced into the aromatic ring by a variety of reagents, eg, H_2SO_4, oleum, SO_3, and $ClSO_3H$, and under a variety of conditions. All these reagents are merely SO_3 carriers, and, not surprisingly, free SO_3 is found to be the most active sulfonating agent. However, the latter has to be used in aprotic solvents. As a result, sulfuric acid, oleum, and chlorosulfonic acid are the preferred sulfonating agents on the manufacturing scale.

The sulfonic acid group can be introduced into molecules containing a variety of other groups such as halogen, hydroxy, acylamino, etc, without interfering with this functionality. Sulfonation is retarded by the presence of deactivating substituents, especially nitro groups. For instance, under normal conditions 2,4-dinitrobenzene cannot be sulfonated. Sulfonation of benzene gives initially the monosulfonated benzene: this is then converted to the *m*-disulfonic acid under more severe conditions or longer reaction times. Sulfonation of toluene leads to a mixture of ortho and para isomers, which can be sulfonated further to toluene-2,4-disulfonic acid.

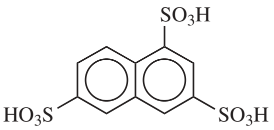
As in the nitration of naphthalene, sulfonation gives the 1-substituted naphthalene. However, because the reverse reaction (desulfonation) is appreciably fast at higher temperatures, the thermodynamically controlled product, naphthalene-2-sulfonic acid, can also be obtained. Thus it is possible to obtain either of the two possible isomers of naphthalene sulfonic acid. Under kinetically controlled conditions naphthalene-1-sulfonic acid [85-47-2] (**82**) is obtained; thermodynamic control gives naphthalene-2-sulfonic acid [120-18-3] (**83**).



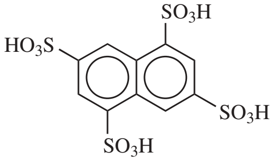
(**82**)

(**83**)

Prolonged heating and stronger reagents lead to the introduction of further sulfonic acid groups into naphthalene. In this way disulfonated and trisulfonated derivatives can be obtained. By careful manipulation of the reaction conditions a high yield of just one isomer is possible, eg, in the preparation of 1,3,6-naphthalenetrisulfonic acid [86-66-8] (**84**). When sulfonic acid groups are introduced into a naphthalene ring, they always enter at a vacant position that is not ortho, para, or peri to another sulfonic acid group. The result of this interesting experimental observation is that only one tetrasulfonated naphthalene [6654-67-7] (**85**) is obtained, and pentasulfonated naphthalenes cannot be obtained by sulfonation.

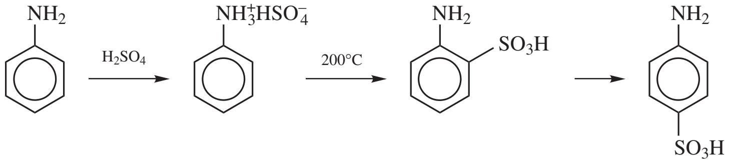


(**84**)

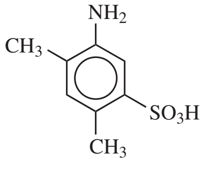


(**85**)

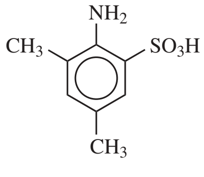
Bake sulfonation is an important variant of the normal sulfonation procedure. The reaction is restricted to aromatic amines, the sulfate salts of which are prepared and heated (dry) at a temperature of approximately 200°C *in vacuo*. The sulfonic acid group migrates to the ortho or para positions of the amine to give a mixture of orthanilic acid [88-21-1] and sulfanilic acid [121-57-3], respectively. This tendency is also apparent in polynuclear systems so that 1-naphthylamine gives 1-naphthylamine-4-sulfonic acid.



The reaction is therefore useful for the introduction of a sulfonic acid group into a specific position. An example where bake sulfonation complements conventional sulfonating procedures is given by the sulfonation of 2,4-dimethylaniline. Conventional sulfonating conditions result in the sulfonic acid group entering the 5-position (directed ortho and para to the methyl groups and meta to the NH_3^+ group) to give the 4,6-dimethylaniline-3-sulfonic acid [6370-23-6] (**86**), whereas bake sulfonation gives the 4,6-dimethylaniline-2-sulfonic acid [88-22-2] (**87**).

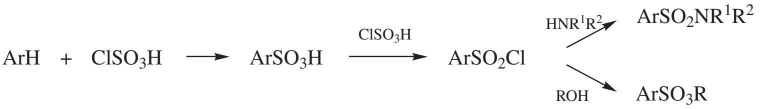


(**86**)



(**87**)

In cases where a large excess of acid is undesirable, chlorosulfonic acid is employed. An excess of chlorosulfonic acid leads to the introduction of a chlorosulfonyl group which is a useful synthon for the preparation of sulfonamides and sulfonate esters.



It is possible to introduce sulfonic acid groups by alternative methods, but these are little used in the dyes industry. However, one worth mentioning is sulfitation, because it provides an example of the introduction of a sulfonic acid group by nucleophilic substitution. The process involves treating an active halogen compound with sodium sulfite. This reaction is used in the purification of *m*-dinitrobenzene.

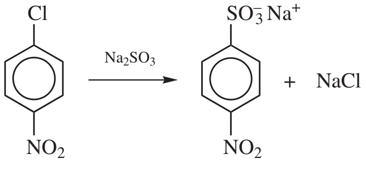


Table 5 lists some intermediates obtained by sulfonation and the sulfonating conditions employed.

Oxidation. This process, ie, the introduction of oxygen into or the removal of hydrogen from a molecule, mainly occurs at an early stage in the syntheses; the more highly substituted molecules are less amenable to oxidation. The processes for manufacturing anthraquinone, phthalic anhydride, phenol, hydroquinone, benzaldehyde, and benzoic acid are virtually all catalytic and sited in dedicated plants. The Hofmann process for making anthranilic acid should also be mentioned as a special example of hypochlorite oxidation.

Table 5. **Intermediates Obtained by Sulfonation**

Product	CAS Registry number	Starting material	Sulfonation process
benzene-1,3-disulfonic acid	[98-48-6]	benzene	30% oleum/180°C
p-toluenesulfonic acid	[104-15-4]	toluene	monohydrate 100°C (100% H_2SO_4)
1-naphthalenesulfonic acid	[85-47-2]	naphthalene	98% H_2SO_4/40°C (96% yield)
2-naphthalenesulfonic acid	[20-18-3]	naphthalene	96% H_2SO_4/165°C (85% yield)
m-nitrobenzenesulfonic acid	[98-47-5]	nitrobenzene	65% oleum/100°C
4-chloro-3-nitrobenzene-sulfonic acid	[121-18-6]	*o*-chloronitro benzene	SO_3 or $ClSO_3H$/solvent
naphthalene-2,7 disul-fonic acid	[92-41-1]	naphthalene-2-sulfonic acid	monohydrate/165°C (65% yield + 25% 2,6)
2-chloro-5-nitrobenzene-sulfonic acid	[96-73-1]	*p*-chloronitro benzene	65% oleum/100°C
2-hydroxy-1-naph-thalenesulfonic acid	[567-47-5]	2-naphthol	SO_3 or $ClSO_3H$/solvent
naphthalene-1,3,6-trisulfonic acid	[86-66-8]	naphthalene-2,7-disulfonic acid	20% oleum/180°C through process
7-hydroxy-1,3-naph-thalene disul-fonic acid[a]	[118-32-1]	2-naphthol-6-sulfonic acid	2-naphthol-6-sulfonic acid
98% H_2SO_4/120°C and separation by fractional salting	3-hydroxy-2,7-naph-thalene disul-fonic acid[b]	[148-75-4]	
7-hydroxy 1,3,6-naphthalene trisul-fonic acid	[6259-66-1]	2-naphthol-6,8-disulfonic acid	40% oleum/120°C through process
sulfanilic acid	[21-57-3]	aniline	dry bake/200°C
aniline-2,5-disulfonic acid	[98-44-2]	metanilic acid	65% oleum/160°C
m-phenylenediamine-4-sulfonic acid	[88-63-1]	*m*-phenylene-diamine	
p-phenylenediamine-2,5-disulfonic acid	[7139-89-1]	*p*-phenylenediamine sulfonic acid	
naphthionic acid	[84-86-6]	1-naphthylamine	dry bake/170°C

1,5-naphthalenedi-sulfonic acid	[117-62-4]	2-naphthylamine-1-sulfonic acid (Tobias acid)	65% oleum/80°C
6-amino-1,3,5-naph-thalenetrisulfonic acid	[55524-84-0]	2-naphthylamine-1-sulfonic acid	65% oleum/80°C
anthraquinone-1-sulfonic acid	[82-49-5]	anthraquinone	20% oleum/HgO catalyst/150°C (75% yield)[c]
anthraquinone-2-sul-fonic acid	[84-48-0]	anthraquinone	20% oleum/150°C (90% yield after 50% conversion)[d]
anthraquinone-1,5-disulfonic acid	[117-14-6]	anthraquinone	65% oleum/HgO catalyst/120°C[e]
p-toluenesulfonyl chloride	[98-59-9]	toluene	$ClSO_3H$/20°C isomer separation $ClSO_3H$/100°C

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[a] G-acid.

[b] R-acid.

[c] Plus 22% anthraquinone for recycle.

[d] Plus anthraquinone for recycle.

[e] After separation 40% yield of 1,5 plus 25% 1,8.

Table 6. **Substituted Naphthols Obtained by Fusion**

Product	CAS Registry number	Starting material
H-acid (1-amino-8-naphthol-3,6-disulfonic acid)	[90-20-0]	1-naphthylamine-3,6,8-trisulfonic acid
J-acid (6-amino-1-naphthol-3-sulfonic acid)	[87-02-5]	2-naphthylamine-5,7-disulfonic acid
gamma acid (7-amino-1-naphthol-3-sulfonic acid)	[90-51-7]	2-naphthylamine-6,8-disulfonic acid
4,6-dihydroxynaphthalene-2-sulfonic acid	[6357-93-3]	7-hydroxynaphthalene-1,3-disulfonic acid (G-acid)
K-acid (8-amino-1-naphthol-3,5-disulfonic acid)	[130-23-4]	1-naphthylamine-4,6,8-trisulfonic acid
Chicago acid (1,8-dihydroxy-naphthalene-2,4-disulfonic acid)	[82-47-3]	naphthasultam-2,4-disulfonic acid
chromotropic acid (1,8-dihydroxy naphthalene-3,6-disulfonic acid)	[148-25-4]	1-naphthol-3,6,8-trisulfonic acid

Fusion / Hydroxylation. The conversion of arylsulfonic acids to the corresponding hydroxy compound is normally effected by heating with caustic soda (caustic fusion). The primary examples are β-naphthol in the naphthalene series and resorcinol in the benzene series; further examples are *m*-aminophenol from metanilic acid and *N,N*-diethyl-*m*-aminophenol from *N,N*-diethylmetanilic acid. In the naphthalene series the hydroxy group is much more commonly introduced at a later stage in the synthesis. Some examples are listed in Table 6, including the most important of the letter acids, ie, acids known by a single letter. In most cases selective hydroxylation takes place at the α-position in α,β-disulfonated naphthalenes, eg, G-acid.

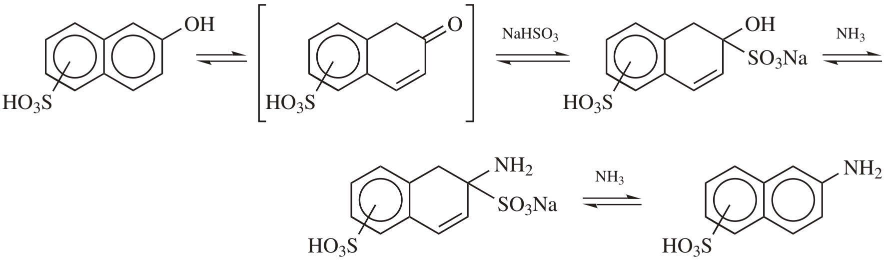
Amination. Amination describes the introduction of amino groups into aromatic molecules by reaction of ammonia or an amine with suitably substituted halogeno, hydroxy, or sulfonated derivatives by nucleophilic displacement. Although reaction and operational conditions vary, the process always involves the heating of the appropriate precursor with excess aqueous ammonia or amine under pressure.

For the amination of aryl halides the reaction proceeds smoothly only when the halogen is activated by electron-withdrawing groups, particularly nitro groups. Examples of suitable precursors are 2-chloronitrobenzene, 4-chloronitrobenzene, 2,4-dinitrochlorobenzene, 1,2-dichloro-4-nitrobenzene, and 1,4-dichloro-2-nitrobenzene, for the respective manufacture of 2-nitroaniline, 4-nitroaniline, 2,4-dinitroaniline, 2-chloro-4-nitroaniline, and 4-chloro-2-nitroaniline. Manufacture of this family of products requires an autoclave operating at temperatures of around 175°C and pressures of 3.5–4.0 MPa (500–600 psi). Sulfonated nitrochlorobenzenes react under less vigorous conditions, and the important 4-nitro-aniline-2-sulfonic acid is manufactured in high yield by amination of 4-chloronitrobenzene-3-sulfonic acid with aqueous ammonia at 120°C and 600 kPa (6 atm).

Catalysts (eg, copper salts) may help with aryl halides of lower activity, but amination of chlorobenzene and 1,4-dichlorobenzene is generally not feasible.

However, the 4-chloro atom of 1,2,4-trichlorobenzene is sufficiently reactive for high temperature amination to yield 3,4-dichloroaniline.

Amination of phenolic derivatives is limited to specially developed catalytic processes for aniline and *m*-toluidine (3). More general conditions apply to amination of naphthols by the Bucherer reaction. Important intermediates made by a Bucherer reaction include Tobias acid and gamma acid.

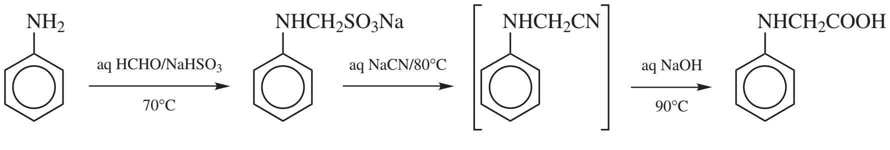


In the anthraquinone series, apart from the special case of the amination of leucoquinizarin, sulfonic acid and nitro are the preferred leaving groups. 1-Aminoanthraquinone is manufactured from anthraquinone-1-sulfonic acid or 1-nitroanthraquinone, and 2-aminoanthraquinone (betamine) from anthraquinone-2-sulfonic acid.

Alkylation. The substitution of a hydrogen atom by an alkyl group can take place at a carbon, nitrogen, or oxygen atom.

N-Alkylation is important in producing a wide range of substituted anilines for use in many dye classes. The products made in the highest quantities, ie, mono- and di-*N*-methyl- and *N*-ethylanilines, are manufactured by continuous catalytic processes, but other products require a wide variety of batch processes. These include alkyl halides, such as ethyl chloride and benzyl chloride, ethylene oxide, which introduces a 2-hydroxyethyl group, acrylonitrile, which introduces a 2-cyanoethyl group, and acrylic acid, which introduces a 2-carboxyethyl group.

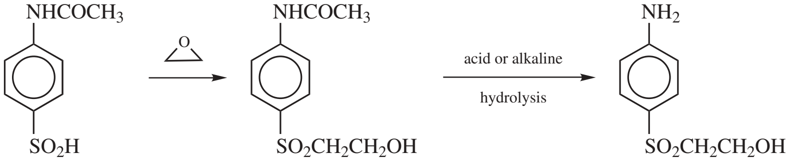
N-Phenylglycine [103-01-5], the key intermediate for indigo, may be manufactured by alkylation of aniline with chloroacetic acid, but it is much more economical, even though three *in situ* stages are required, to use formaldehyde as the alkylating agent.



N-Alkyl and *N*-aryl substituted naphthylamines are also important, eg, letter acid derivatives, but are usually manufactured by the Bucherer reaction.

O-Alkylation is comparable to *N*-alkylation, but since the sodium salts are water-soluble it is most convenient to treat the phenol or naphthol in aqueous caustic solution with dimethyl sulfate or diethyl sulfate. These are comparatively expensive reagents, and therefore, alkoxy groups are introduced at a prior stage by a nucleophilic displacement reaction whenever possible.

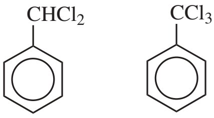
Manufacture of alkylsulfones, important intermediates for metal-complex dyes and for reactive dyes, also depends on *O*-alkylation. An arylsulphinic acid in an aqueous alkaline medium is treated with an alkylating agent, eg, alkyl halide or sulfate, by a procedure similar to that used for phenols. In the special case of β-hydroxyethylsulfones (precursors to vinylsulfone reactive dyes) the alkylating agent is ethylene oxide or ethylene chlorohydrin.



C-Alkylations may be discussed under the headings of alkene reactions and *N*-alkyl rearrangements. The isopropylation of benzene and naphthalene are two important examples of alkylation with alkenes (see ALKYLATION). Manufacture of *p*-butylaniline, by heating *N*-butylaniline with zinc chloride, typifies the rearrangement reaction appropriate to C_4 and higher alkyl derivatives.

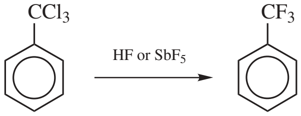
Halogenation. Halogenation is the process of introducing one or more halogen atoms (F, Cl, or Br) into an organic molecule. The two most important halogens, chlorine and bromine, are usually introduced into benzenoid aromatics by direct halogenation. In contrast, they are frequently introduced into the naphthalene nucleus using the Sandmeyer or Gattermann reactions. When halogens are introduced directly in their elemental forms, ie, chlorine gas or bromine liquid, a catalyst is required, usually the corresponding iron III halide ($FeCl_3$ or $FeBr_3$). The iron catalyst is added either directly or is formed *in situ* by the addition of iron to the reaction mixture ($2\,Fe + 3\,X_2 \longrightarrow 2FeX_3$). In the presence of catalyst, halogenation proceeds by electrophilic attack of the halonium ion ($FeX_3 + X_2 \longrightarrow X^+ + FeX_4^-$ at the aromatic nucleus to give the corresponding halobenzene. Thus benzene is chlorinated by passing a stream of chlorine gas into benzene containing a catalytic amount of $FeCl_3$ at approximately 30°C. Similarly, toluene is chlorinated to give a mixture of *o*- and *p*-chlorotoluenes that is separated by fractional distillation. Predictably, deactivated benzenes, eg, nitrobenzene, require higher temperatures (>50°C) for reaction to occur. In contrast, activated systems such as phenols and anilines require no catalyst, and the reaction proceeds readily at room temperature. In fact, phenols are so active that dilute sodium hypochlorite (NaOCl) solutions must be used to obtain the monochlorinated derivative, and aromatic amines have to be deactivated by acetylation to avoid over-chlorination.

If the aromatic hydrocarbon is substituted by alkyl groups, then, under the right conditions, substitution can occur in the side chain. The mechanism involves radicals, and therefore the conditions for ionic nuclear halogenation must be avoided, eg, no Lewis acid catalysts (FeX_3) must be present. As a result these reactions are carried out in iron-free reaction vessels (enamel or glass-lined). Higher temperatures, which facilitate homolytic cleavage of the halogen, are generally required than for the ionic reaction and the presence of radical initiators, eg, uv light or benzoyl peroxide, is beneficial. Benzyl chloride, a useful alkylating agent, may thus be obtained from toluene. Further chlorination of benzyl chloride gives a mixture of the dichloro derivative and the trichloro derivative.



The latter two compounds are important sources of benzaldehyde and benzoyl chloride/benzoic acid respectively (see CHLOROCARBONS AND CHLOROHYDROCARBONS, BENZYL CHLORIDE, BENZAL CHLORIDE, AND BENZOTRICHLORIDE).

Fluorination and iodination reactions are used relatively little in dye synthesis. Fluorinated species include the trifluoromethyl group, which can be obtained from the trichloromethyl group by the action of hydrogen fluoride or antimony pentafluoride, and various fluorotriazinyl and pyrimidyl reactive systems for reactive dyes, eg, Cibacron F dyes.



Hydrolysis. The general process definition for hydrolysis embraces all double-decomposition reactions between water (usually in the form of acid or alkali solutions of a wide range of strengths) and an organic molecule.

The main type of hydrolysis reaction is that of halogenoaryl compounds to hydroxyaryl compounds, eg, the aqueous caustic hydrolysis of *o*- and *p*-chloronitrobenzene derivatives to nitrophenols. Another important reaction is the hydrolysis of *N*-acyl derivatives back to the parent arylamine, where the acyl group is frequently used to protect the amine.

Condensation. This term covers all processes, not previously included in other process definitions, where water or hydrogen chloride is eliminated in a reaction involving the combination of two or more molecules. The important condensation reactions are nitrogen and sulfur heterocycle formation, amide formation from acid chlorides, formation of substituted diphenylamines, and miscellaneous cyclizations.

A significant group of carbonamides are the Naphtol products formed by condensation of 2-hydroxy-3-naphthoic acid (via its acid chloride) with a wide range of arylamines. The simplest example, Naphtol AS from aniline, is typical, and manufacture is accomplished by suspending the acid in a solvent such as toluene, preforming the acid chloride by addition of phosphorus trichloride, and then adding the aniline.

Sulfonamides, as a class, are simple to manufacture once the isolation conditions for the moderately stable sulfonyl chloride have been established. Basically all processes involve the addition of the sulfonyl chloride paste to excess ammonia or amine in aqueous solution. The product can usually be filtered off in a reasonably pure form with only the hydrolysis product remaining in the liquor.

The reaction of substituted chloronitrobenzenes with arylamines to form substituted diphenylamines is typified by 4-nitrodiphenylamine-2-sulfonic acid where 4-chloronitrobenzene-3-sulfonic acid (PN salt) is condensed with aniline in an aqueous medium at 120°C and 200 kPa (2 atm) in the presence of alkaline buffer at low pH to avoid the competing hydrolysis of the PN salt.

Alkoxylation. The nucleophilic replacement of an aromatic halogen atom by an alkoxy group is an important process, especially for production of methoxy-containing intermediates. Alkoxylation is preferred to alkylation of the phenol wherever possible, and typically involves the interaction of a chloro compound, activated by a nitro group, with the appropriate alcohol in the presence of alkali. Careful control of alkali concentration and temperature are essential, and formation of by-product azoxy compounds is avoided by passing air through the reaction mixture (21).

Carboxylation. This is the process of introducing a carboxylic acid group into a phenol or naphthol by reaction with carbon dioxide under appropriate conditions of heat and pressure. Important examples are the carboxylation of phenol and 2-naphthol to give salicylic acid and 2-hydroxy-3-naphthoic acid, respectively.

Acylation. Somewhat analogous to alkylation, the substitution of a hydrogen atom by an acyl group can take place at a carbon, nitrogen, or oxygen atom. The most common method of *C*-acylation is the Friedel-Craft reaction (qv) between an acyl chloride or diacid anhydride and an aromatic residue. Typically, *o*-carboxybenzophenones are formed by heating benzenoid substrates, phthalic anhydride, and aluminum chloride. These are normally cyclized to anthraquinone using concentrated sulfuric acid.

N-Acetyl and *N*-benzoyl derivatives are formed by treating the arylamine in water with acetic anhydride or benzoyl chloride. Apart from the occasional requirement of an *N*-acyl group in the final product, the *N*-acetyl group is frequently used in the manufacturing chain to temporarily protect the amine group during nitration, chlorination or chlorosulfonation; the acetyl group is readily removed by hydrolysis. Protection of *o*-aminophenols in this way is a slight variation since the *N*-acetyl derivative ring closes to form the 2-methylbenzoxazolone. Selective acetylation of diamines is utilized in the manufacture of 4-acetylamino-2-amino-benzenesulfonic acid from *m*-phenylenediamine sulfonic acid, and 5-acetylamino-2-aminobenzenesulfonic acid from *p*-phenylenediamine sulfonic acid. In these cases use is made of the increased difficulty of acylating the amino group sterically hindered by a bulky ortho substituent. The corresponding dichlorotriazinyl derivatives, using cyanuric chloride as the acylating agent, are important reactive dye intermediates.

O-Acylation is used to modify side-chain properties, and is typically achieved by heating an *N*-β-hydroxyethylaniline with acetic anhydride to form the *O*-acetoxy derivative.

Phosgenation. Reaction of phosgene with arylamines to form ureas, and with reactive aryl species to form substituted benzophenones, are special cases of acylation. They are dealt with separately since a more specialized plant is required than for other acylations. Urea formation takes place readily with water-soluble arylamines by simply passing phosgene through a slightly alkaline solution. An important example is carbonyl-J-acid from J-acid.

Esterification. The formation of an ester from an acid (or its derivative) and an alcohol is of limited application since carboxylic esters are comparatively rare substituents in dyes. Esters of *N*-β-hydroxyethylanilines are important intermediates for azo disperse dyes for polyester. Another example is methyl anthranilate, formed by the classical esterification of anthranilic acid using methanol and sulfuric acid.

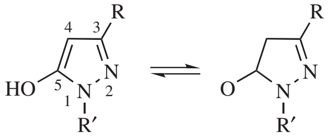
Figure 6 summarizes the preparation of key intermediates from benzene, and Figure 7 shows a dye synthesis from benzene. Figures 8 and 9 show the preparation of key intermediates from naphthalene and β-naphthol.

7.2. Chemistry of Aromatic Heterocycles.

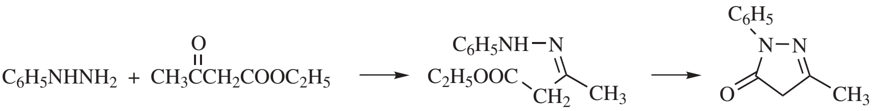
In contrast to the benzenoid intermediates, it is unusual to find a heterocyclic intermediate that is synthesized via the parent heterocycle. They are synthesized from acyclic precursors.

The most important heterocycles are those with five- or six-membered rings; these rings may be fused to other rings, especially a benzene ring. Nitrogen, sulfur, and to a lesser extent oxygen, are the most frequently encountered heteroatoms. They are often considered in two groups: those containing only nitrogen, such as pyrazolones, indoles, pyridones, and triazoles which, except for triazoles, are used as coupling components in azo dyes, and those containing sulfur (and also optionally nitrogen), such as thiazoles, thiophenes, and isothiazoles, that are used as diazo components in azo dyes. Triazines are treated separately since they are used as the reactive system in many reactive dyes.

N-Heterocycles. *Pyrazolones.* Pyrazolones are used as coupling components since they couple readily at the 4-position under alkaline conditions to give important azo dyes in the yellow-orange shade area.



The most important synthesis of pyrazolones involves the condensation of a hydrazine with a β-ketoester such as ethyl acetoacetate. Commercially important pyrazolones carry an aryl substituent at the 1-position, mainly because the hydrazine precursors are prepared from readily available and comparatively inexpensive diazonium salts by reduction. In the first step of the synthesis the hydrazine is condensed with the β-ketoester to give a hydrazone: heating with sodium carbonate then effects cyclization to the pyrazolone. In practice the condensation and cyclization reactions are usually done in one pot without isolating the hydrazone intermediate.



Pyridones. Pyridine itself has little importance as a dyestuff intermediate. However, its 2,6-dihydroxy derivatives have achieved prominence in recent

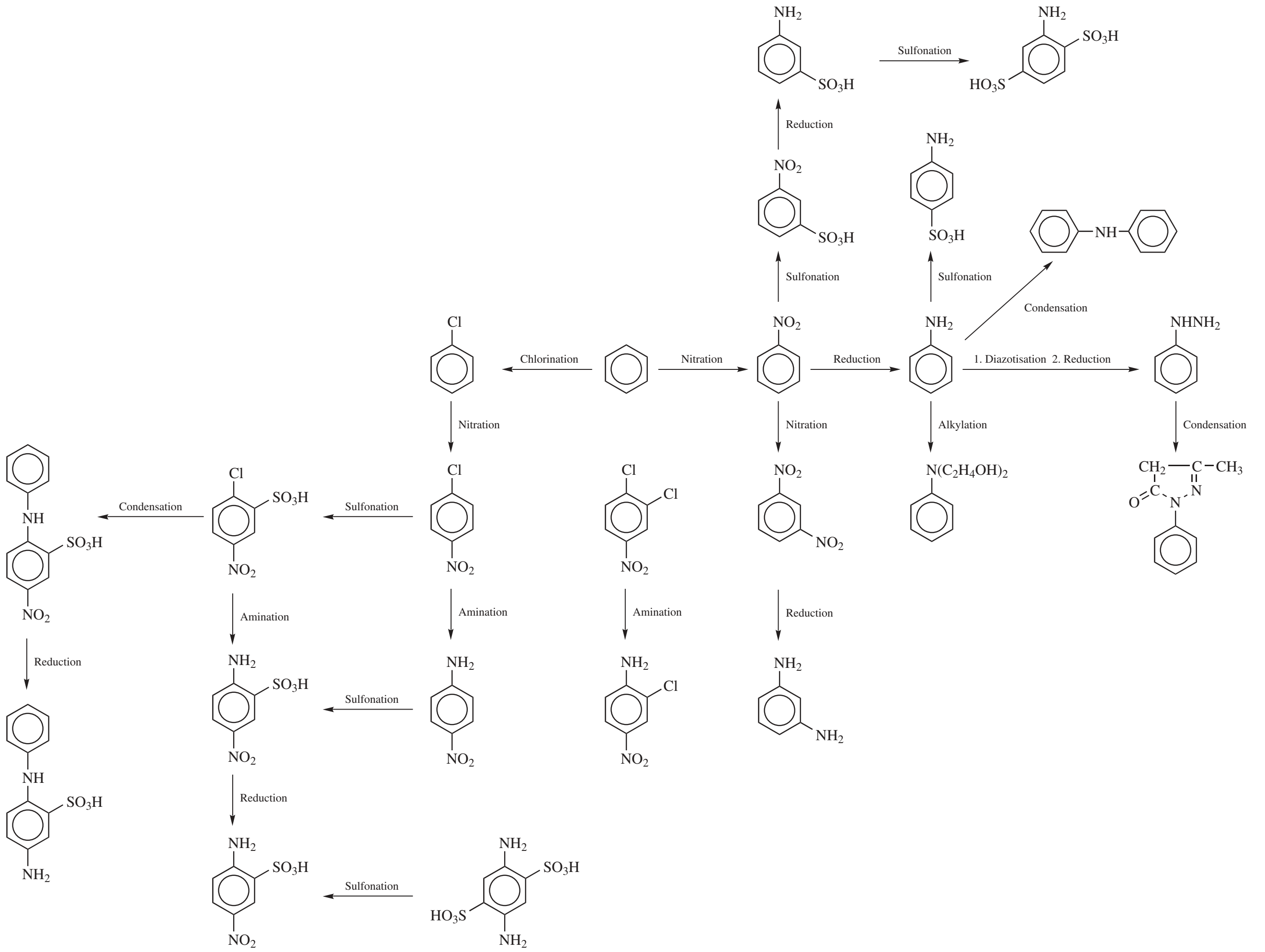


Fig. 6. Key intermediates derived from benzene. The alkylation reaction shown employs ethylene oxide. Hydrazine condenses with acetoacetic acid to form the heterocyclic ring shown.

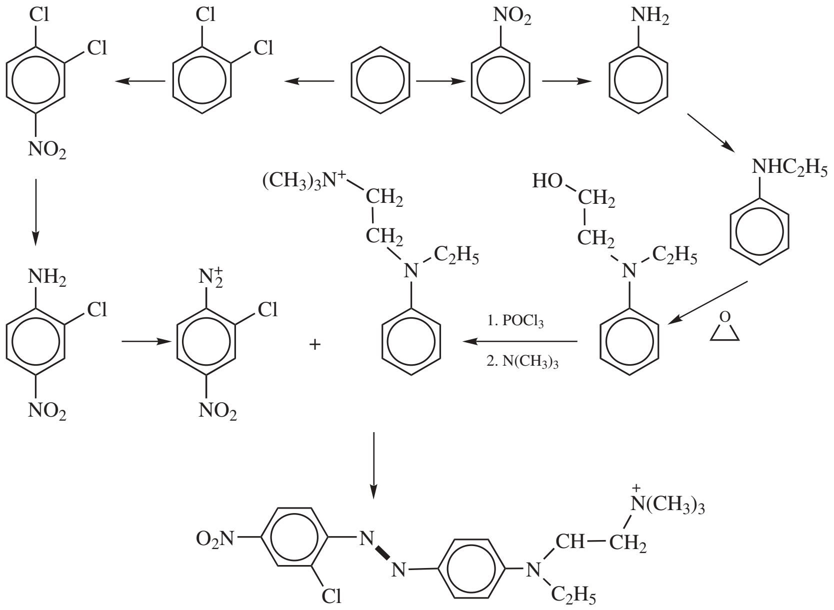
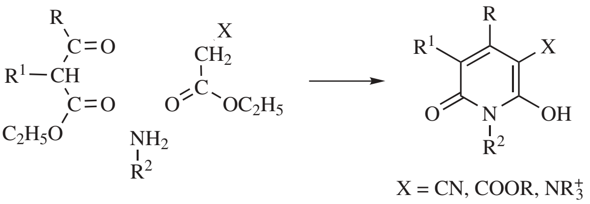


Fig. 7. Synthesis of a dye, CI Basic Red 18, from benzene.

years as coupling components for azo dyes, particularly in the yellow shade area.

The most convenient synthesis of 6-hydroxy-2-pyridones is by the condensation of a β-ketoester, eg, ethyl acetoacetate, with an active methylene compound, eg, malonic ester, cyanoacetic ester, and an amine. The amine can be omitted if an acetamide is used and in some cases this modification results in a higher yield.



R is usually alkyl or less frequently aryl; R^1 is H, and the R^2 group can be alkyl, aryl, and even an amino or a hydroxy group. By virtue of the synthetic method, X is an electron-withdrawing group, eg, CN, CO_2R, although simple derivatives, eg, $X = CONH_2$, H, are readily obtained by hydrolysis. Dyes from pyridones, in which X is an ammonium group (from $R_3N^+CH_2CONH_2$), are used for polyacrylonitrile fibers. An interesting situation is encountered in the synthesis of the pyridone (**88**) using malononitrile as the active methylene compound. Here an amine is not required since the nitrogen is provided by the nitrile

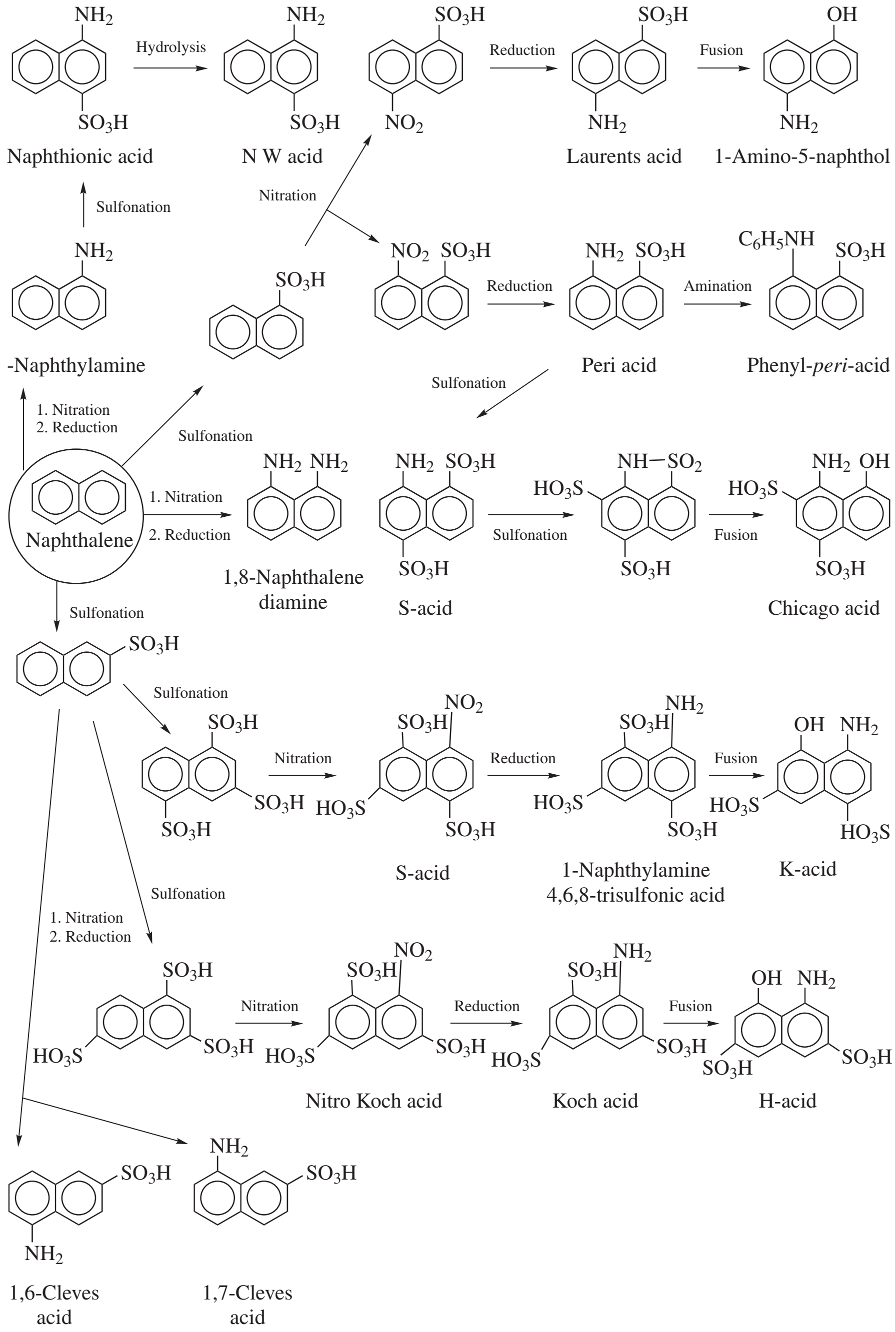


Fig. 8. Key intermediates derived from naphthalene.

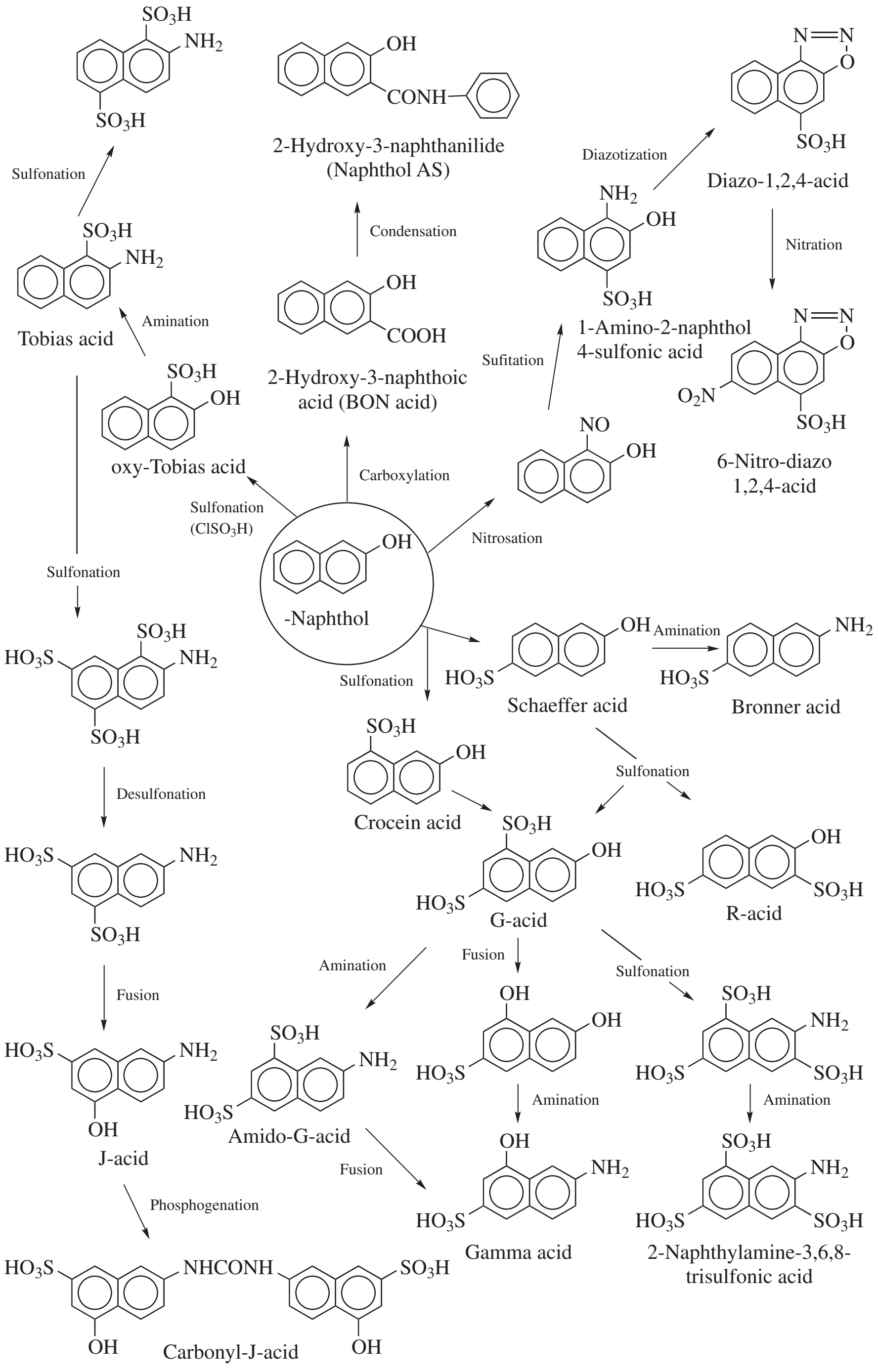
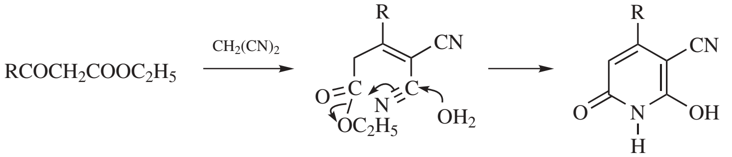


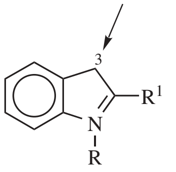
Fig. 9. Key intermediates derived from β-naphthol.

which undergoes a facile cyclization from the nitrile ester intermediate.

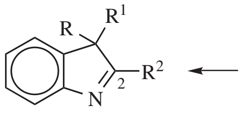


(**88**)

Indoles. Indoles (**89**) are used as coupling components to give azo dyes; the structurally related indolenines (**90**) are also employed as intermediates in cyanine dyes. The arrows indicate coupling positions. In (**89**) R = H, aryl, alkyl; R^1 = aryl, alkyl; in (**90**) R, R^1 = aryl, alkyl; and R^2 = alkyl.

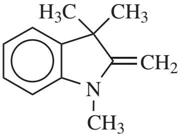


(**89**)



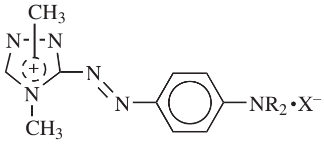
(**90**)

The majority of commercial indoles are synthesized by way of the Fischer-Indole synthesis, which involves the rearrangement of phenylhydrazones to indoles and their derivatives. Such hydrazones must contain at least one α-hydrogen for rearrangement to occur and acid catalysts such as $ZnCl_2$, HCl, polyphosphoric acid, and H_2SO_4 are used to effect the rearrangement. Fischer's Base [118-12-7] (**91**) is one of the most important indole derivatives.



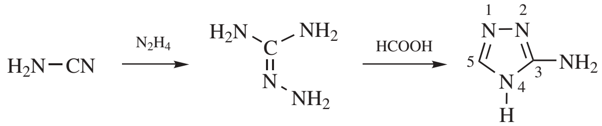
(**91**)

Triazoles. The triazoles are fairly representative of five-membered heterocycles containing three heteroatoms. The only other commercially important heterocycles containing three heteroatoms are 5-amino-1,2,4-thiadiazoles, and the isomeric 2-amino-1,3,4-thiadiazoles. Heterocycles containing more heteroatoms are not generally found in dyestuffs, and even triazoles are not of widespread importance, although they do provide some useful red dyes, eg, (**92**) for polyacrylonitrile fibers.



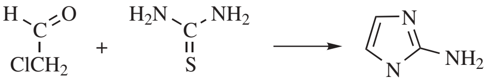
(**92**)

The most important triazole is 3-amino-1,2,4-triazole itself, used in the synthesis of diazahemicyanine dyes. The preparation of 3-amino-1,2,4-triazole [61-82-5] (**93**) is simple, using readily available and quite inexpensive starting materials. Thus cyanamide [420-04-2] reacts with hydrazine, to give aminoguanidine [54852-84-5] which then condenses with formic acid. Substituents in the 5-position are introduced merely by altering the carboxylic acid used.



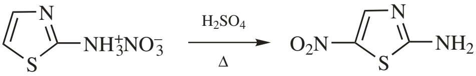
(**93**)

Sulfur and Sulfur–Nitrogen Heterocycles. Aminothiazoles. In contrast to the pyrazolones, pyridones, and indoles just described, aminothiazoles are used as diazo components. As such they provide dyes that are more bathochromic than their benzene analogues. Thus aminothiazoles are used chiefly to provide dyes in the red-blue shade areas. The most convenient synthesis of 2-aminothiazoles is by the condensation of thiourea with an α-chlorocarbonyl compound; for example, 2-aminothiazole [96-50-4] (**94**) is prepared by condensing thiourea [62-56-6] with α-chloroacetaldehyde [107-20-0] both readily available intermediates.

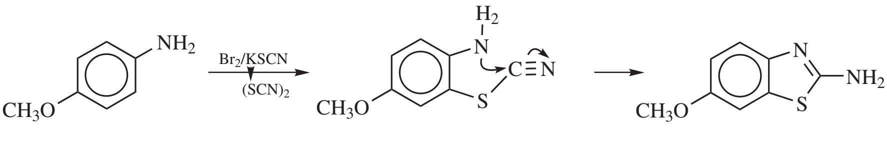


(**94**)

Substituents can be introduced into the thiazole ring either by using suitably substituted precursors or by direct electrophilic attack on the ring. An interesting example of the latter method is the preparation of 2-amino-5-nitrothiazole [121-66-4] from the nitrate salt of 2-aminothiazole.

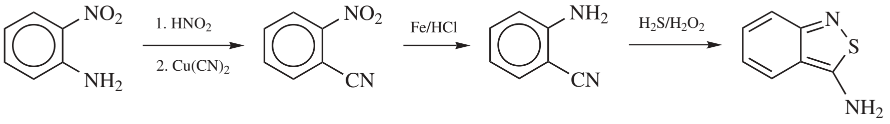


Aminobenzothiazoles. These compounds are prepared somewhat differently than the thiazoles. The thiazole ring is annelated onto a benzene ring, usually via an aniline derivative. Thus 2-amino-6-methoxybenzothiazole [1747-60-0] (**95**) is obtained from *p*-anisidine [104-94-9] and thiocyanogen. The thiocyanogen, which is formed *in situ* from bromine and potassium thiocyanate (the Kaufman reaction), reacts immediately with *p*-anisidine to give the thiocyanate derivative, which spontaneously ring closes to the aminobenzothiazole.

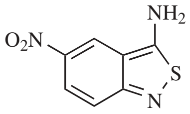


(**95**)

Benzoisothiazoles. 5-Aminoisothiazoles are relatively difficult to prepare cheaply, but they are used as diazo components in magenta dyes for Dye Diffusion Thermal Transfer, D2T2. However, the benzo-homologues are far easier to prepare and are important diazo components. Aminobenzoisothiazoles give dyes that are even more bathochromic than the corresponding dyes from aminobenzothiazoles. Aminobenzoisothiazoles [2400-12-6] can be prepared from *o*-nitroanilines through the intermediacy of *o*-cyanoanilines.

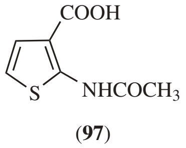


The most important commercial benzoisothiazole is the 3-amino-5-nitrobenzoisothiazole [14346-19-1] (**96**) prepared by an analogous route but starting from 2-cyano-4-nitroaniline [17420-30-3].

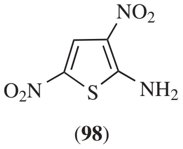


(**96**)

Thiophenes. The most important thiophenes, ie, 2-aminothiophenes, are used as diazo components for azo dyes and are capable of producing very bathochromic dyes, eg, greens, having excellent properties. Part of the reason for their late arrival on the commercial scene has been the difficulty encountered in attaining a good synthetic route. However, this problem has been overcome by ICI (22). The synthetic route is a very flexible so that a variety of protected 2-amino-thiophenes can be obtained merely by altering the reaction conditions or alternatively by stopping the reaction at an intermediate stage. Thus the initially formed thiophene [51419-38-4] (**97**) can be converted to the useful 2-amino-3,5-dinitrothiophene [2045-70-7] (**98**) by either of two routes.

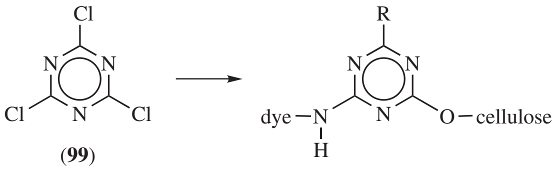


(**97**)



(**98**)

Triazines. The most commercially important triazine is 2,4,6-trichloro-*s*-triazine [108-77-0] (cyanuric chloride, (**99**)). Cyanuric chloride has not achieved prominence because of its value as part of a chromogen but because of its use for attaching dyestuffs to cellulose, ie, as a reactive group (see Dyes, reactive). This innovation was first introduced by ICI in 1956, and since then other active halogen compounds have been introduced.


(99)

On the large scale, cyanuric chloride is produced by the trimerization of cyanogen chloride. The cyanogen chloride is produced by chlorination of hydrogen cyanide and is trimerized by passing it over charcoal impregnated with an alkaline-earth metal chloride at a high temperature (250–480°C).

$$3\,\mathrm{H{-}C{\equiv}N} \xrightarrow{\mathrm{Cl_2}} 3\,\mathrm{Cl{-}C{\equiv}N} \longrightarrow (\mathbf{99})$$

8. Equipment and Manufacture

The basic steps of dye (and intermediate) manufacture are shown in Figure 10. There are usually several reaction steps or unit processes.

The reactor itself, in which the unit processes to produce the intermediates and dyes are carried out, is usually the focal point of the plant, but this does not mean that it is the most important part of the total manufacture, nor that it absorbs most of the capital or operational costs. Operations subsequent to reaction are often referred to as work-up stages. These vary from product to product with intermediates (used without drying wherever practicable) needing less finishing operations than colorants.

The reactions for the production of intermediates and dyes are carried out in bomb-shaped reaction vessels made from cast iron, stainless steel, or steel lined with rubber, glass (enamel), brick, or carbon blocks. Wooden vats are also still used in some countries, eg, India. These vessels have capacities of 2–40 m^3 (ca 500–10,000 gal) and are equipped with mechanical agitators, thermometers or temperature recorders, condensers, pH-probes, etc, depending on the nature of the operation. Jackets or coils are used for heating and cooling by circulating through them high boiling fluids (eg, hot oil, or Dowtherm), steam, or hot water to raise the temperature, and air, cold water, or chilled brine to lower it. Unjacketed vessels are often used for aqueous reactions, where heating is affected by direct introduction of steam, and cooling by addition of ice or by heat exchangers. The reaction vessels normally span two or more floors in a plant to facilitate ease of operation (see REACTOR TECHNOLOGY).

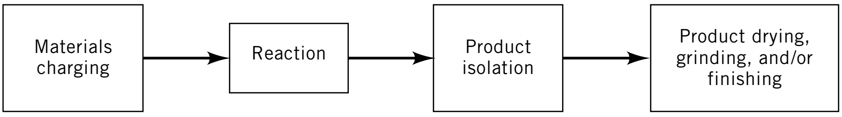


Fig. 10. Operation sequence in dye and intermediate manufacture.

Products are transferred from one piece of equipment to another by gravity flow, pumping, or by blowing with air or inert gas. Solid products are separated from liquids in centrifuges, on filter boxes, on continuous belt filters, and perhaps most frequently, in various designs of plate-and-frame or recessed plate filter presses. The presses are dressed with cloths of cotton, Dynel, polypropylene, etc. Some provide separate channels for efficient washing, others have membranes for increasing the solids content of the presscake by pneumatic or hydraulic squeezing.

The plates and frames are made of wood, cast iron, or now usually hard rubber, polyethylene, and polyester.

When possible, the intermediates are taken for the subsequent manufacture of other intermediates or dyes without drying because of savings in energy costs and handling losses. There are, however, many cases where products, usually in the form of pastes discharged from a filter, must be dried. Even with optimization of physical form, the water content of pastes varies from product to product in the range of 20 to 80%. Where drying is required, air or vacuum ovens (in which the product is spread on trays), rotary dryers, spray dryers, or less frequently drum dryers (flakers) are used. Spray dryers have become increasingly important. They need little labor and accomplish rapid drying by blowing concentrated slurries, eg, reaction masses, through a small orifice into a large volume of hot air. Dyes, especially disperse dyes, that require wet-grinding as the penultimate step, are now often dried this way. In this case their final standardization, ie, addition of desired amounts of auxiliary agents and solid diluents, is achieved in the same operation (see DRYING).

The final stage in dye manufacture is grinding or milling. Dry grinding is usually carried out in impact mills (Atritor, KEK, or ST); considerable amounts of dust are generated, and well-established methods are available to control this problem. Dry grinding is an inevitable consequence of oven drying, but more modern methods of drying, especially continuous drying, allow the production of materials that do not require a final comminution stage. The ball mill, consisting of a rotating or vibrating hollow cylinder partially filled with hard balls, has always been of limited use for dry grinding because of product removal problems. Although historically significant for wet milling, the ball mill has been superseded by sand or bead mills. Wet milling has become increasingly important for pigments and disperse dyes. Many recently patented designs, particularly from Draiswerke GmbH and Gebruder Netzsch Maschinfabrik, consist of vertical or horizontal cylinders equipped with high speed agitators of various configurations with appropriate continuous feed and discharge arrangements. The advantages and disadvantages of vertical and horizontal types have been discussed (23); these are so finely balanced as to lead to consideration of tilting versions to combine the advantages of both.

In the past the successful operation of batch processes depended mainly on the skill and accumulated experience of the operator. This operating experience was difficult to codify in a form that enabled full use to be made of it in developing new designs. The gradual evolution of better instrumentation, followed by the installation of sequence control systems, has enabled much more process data to be recorded, permitting maintenance of process variations within the minimum possible limits.

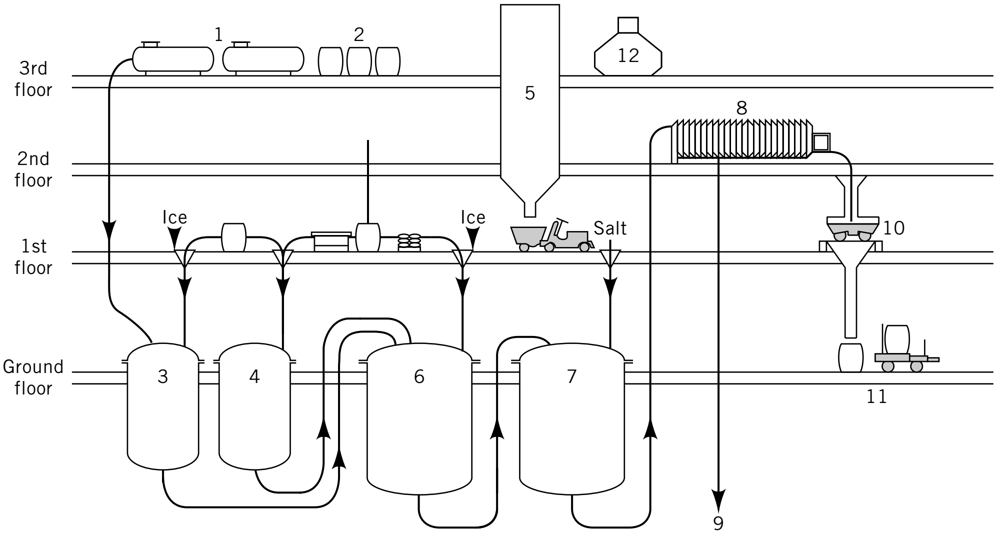


Fig. 11. Layout of azo dye manufacturing plant. 1, storage tanks for liquid starting materials; 2, storage drums for solid starting materials; 3, diazotization vessel; 4, coupling component vessel; 5, ice machine; 6, coupling vessel; 7, isolation vessel; 8, filter presses; 9, filtrate to waste liquor treatment plant; 10, dryers; 11, emptying of dyestuffs to go to the mill; 12, outgoing air purification plant.

Full computerization of multiproduct batch plants is much more difficult than with single-product continuous units because the control parameters vary fundamentally with respect to time. The first computerized azo (24) and intermediates (25) plants were brought on stream by ICI Organics Division (now Zeneca Specialties) in the early 1970s, and have now been followed by many others. The additional cost (ca 10%) of computerization has been estimated to give a saving of 30 to 45% in labor costs (26). However, highly trained process operators and instrument engineers are required. Figure 11 shows the layout of a typical azo dye manufacturing plant.

9. Economic Aspects

Early this century, about 85% of world dyes requirements were manufactured in Germany, with other European countries (Switzerland, UK, and France) accounting for a further 10%. Seventy years and two world wars have seen dramatic changes in this pattern. Table 7 shows that, in weight terms, the Western European share of world production had moved to 50% by 1938 and 40% by 1974. However, since a large part of U.S. manufacture and some of "others" is based on Western European subsidiaries, their overall share remains at over 50%. Since 1974 many of the national figures have not been published, but those that are available indicate that 1974 was the peak production year of the 1970s, with 1975 being the nadir. World recession caused a 20% slump in production which has now been more than recovered.

Table 7. **World Dyestuff Production Trends, 10^3 t**

Year	W. Europe	U.S.	Eurasia[a]a	Japan	Others	Total
1938	110	37	35		28	210
1948		110				
1958	112	80	127		27	346
1966	191	130		49		
1974	300	138	200+	68	44	750+

[a] Eastern Europe, former USSR, and China.

Consequently, the figures of Table 7 are still applicable to the present day. More recent independent reviews (27,28) indicate a slightly lower world output of 750,000 to 800,000 t/yr. With the present state of the world economy in 1993 the growth rate for the industry is likely to be as low as 2–3%, but even this low figure represents something like an additional 20,000 t/yr. The major dye producing countries and companies in Western Europe are shown in Table 8.

Divergent post-war developments within the three principal German companies, Bayer, BASF, and Hoechst (including Cassella which is 75% owned by Hoechst) have led to contrasting profiles. In common with ICI, development of their dyes businesses, representing less than 5% of a total chemicals business, must be seen in the wider context of both heavy chemicals (including plastics and fibers) and fine/specialty chemicals (including dyes). Bayer's strength in intermediates manifested itself in a DM 500 million joint investment with CIBA-GEIGY for new capacity. This Schelde-Chemie plant at Brunsbuttel is by far the largest single investment in new dye/intermediate capacity that the Western world has seen since its main manufacturing bases were established in the 1930s and 1940s. Establishment of an important new works on the Elbe estuary will significantly lessen the effluent load on the Rhine, close to which most of the Swiss and the German industries have been based. Unlike the

Table 8. **West European Dyestuff Production Estimates**[a]

Country	Company	Production, 10^3 t	Value, 10^6 \$
West Germany		148	976
	Bayer		
	BASF		
	Hoechst		
UK		54	268
	ICI		
Switzerland		30	370
	CIBA-GEIGY		
	Sandoz		
France		31	147
Italy		15	62
Spain		15	42
Belgium		6	23
rest of Western Europe		1	4
Total		*300*	*1892*

[a] 1974 Data extrapolated to 1993 as explained in the tex

Germans and the British, the Swiss have confined themselves to their original fine chemicals base, so that dyes represent 20–30% of their chemical industry. This must, however, be continually decreasing in the face of more rapidly expanding pharmaceuticals and agrochemicals sectors. They export 80% of their dye production, compared with 65% for UK and 50% for Germany.

Dyes production in the United States has remained much more fragmented than that of European countries. Manufacture is shared between at least 10 manufacturers rather than three or four for each European country. All European majors have a significant manufacturing presence in the United States, gradually replacing exports from Europe. The demise of the long-standing Du Pont dye business in 1979, the withdrawal by American Cyanamid in 1980, the liquidation of the American Color and Chemical business in 1982, and the takeover of the Sodyeco Division of the Martin-Marietta Corporation by Sandoz in 1983, have left manufacturers with wide product ranges. Eastman Chemical Products, a significant producer of disperse dyes, with a restricted approach stemming from its association with a dominant photographic colors manufacturer (Eastman Kodak), has sold its disperse dye line to CIBA-GEIGY. Atlantic has been acquired by Crompton and Knowles.

In the United States during the 1970s and 1980s, reactive dyes (mostly azo) increased, whereas anthraquinone vat dyes decreased. The most notable change is the increase in indigo dyes, which may be as high as 10 million kilograms owing to the popularity of blue jeans.

A historically fragmented Japanese industry, with rapid growth to meet internal demand, changed in 1979 with an agreement by its five principal manufacturers (Mitsubishi, Sumitomo, Nippon Kayaku, Mitsui Toatsu, and Hodogaya) to the formation of a cartel to coordinate research as well as manufacture. Successful operation of this cartel could have profound effects on the international situation by the end of the twentieth century.

Comparatively little is known of manufacture in China and the former Eastern block countries, although their aim must be to satisfy all their own requirements. The signs are that they need to import technology to hasten the process toward self-sufficiency. They are currently significant importers of dyes, although Czechoslovakia in particular, more recently joined by China, does export a limited number of intermediates. These countries were the only ones to announce large-scale investment in new dye-manufacturing capacity for the 1980s. These are a 4000 t/yr disperse dye plant and a 2000 t/yr leather dye plant in the former USSR, both using Montedison/ACNA technology. The Italian group is also reported to be providing know-how for a dyestuff finishing plant to be built in northeast China. Manufacture in India, South America, and Mexico is mainly through subsidiaries, or partly owned companies associated with the main European companies. Within Far Eastern countries, other than Japan, a large number of small manufacturing facilities are evolving, especially in Taiwan and South Korea.

10. Health and Safety Factors

10.1. Toxicology and Registration. The toxic nature of some dyes and intermediates has long been recognized. Acute, or short-term, effects are generally well known. They are controlled by keeping the concentration of the chemicals in the workplace atmosphere below prescribed limits and avoiding physical contact with the material. Chronic effects, on the other hand, frequently do not become apparent until after many years of exposure. Statistically higher incidences of benign and malignant tumors, especially in the bladders of workers exposed to certain intermediates and dyes, were recorded in dye-producing countries during the period 1930–1960. The specific compounds involved were 2-naphthylamine [91-59-8], 4-aminobiphenyl [92-67-1], benzidine (4,4′-diaminobiphenyl) [92-87-5], fuchsine [632-99-5] (CI Basic Violet 14), auramine [2465-27-2] (CI Solvent Yellow 2). There is considerable evidence that metabolites of these compounds are the actual carcinogenic agents (29,30). Strict regulations concerning the handling of known carcinogens have been imposed in most industrial nations. In the United States the regulations (31) caused virtually all the dye companies to discontinue use of the compounds. Other actual or suspected carcinogens, such as the nitrosamines, or *N*-nitroso compounds (30,32) (see *N*-NITROSAMINES), polycyclic hydrocarbons, alkylating agents (30,33), and other individual compounds, such as the dichromates, should be considered in the wider context of industrial chemistry rather than as dye intermediates (see COLORANTS FOR FOODS, DRUGS, COSMETICS, AND MEDICAL DEVICES; INDUSTRIAL HYGIENE AND TOXICOLOGY).

The positive links between benzidine derivatives and 2-naphthylamine with bladder cancer prompted the introduction of stringent government regulations to minimize such occurrences in the future. Currently, the three principal regulatory agencies worldwide are European Core Inventory (ECOIN) and European Inventory of Existing Commercial Substances (EINECS) in Europe, Toxic Substances Control Act (TOSCA) in the United States, and Ministry of Technology and Industry (MITI) in Japan. Each of these has its own set of data and testing protocols for registration of a new chemical substance. For registration in the European Community (EEC) the following items are required: (*1*) identity of the substance; (*2*) information on the substance; (*3*) physicochemical properties of the substance; (*4*) toxicological studies; (*5*) ecotoxicological studies; and (*6*) possibility of rendering the substance harmless. Items (*1*) and (*2*) refer to the chemical structure of the substance (or its method of preparation if the structure is unknown) and information on its appearance.

Physicochemical properties required include melting/boiling point, vapor pressure, solubility, and flammability/explosion characteristics. The toxicological studies include acute toxicity tests, oral, inhalation, and dermal; skin and eye irritation; skin sensitization; subacute toxicity, oral, inhalation, and dermal; and mutagenicity tests. *In vitro:* reverse mutation assay (Ames test) on Salmonella typhimurium and/or Escherichia coli and mammalian cytogenic test. *In vivo:* mouse micronucleus test.

Finally, the ecotoxicological studies, designed to assess the impact of the substance on the environment, embrace acute toxicity tests to fish and Daphnia, and a battery of tests for the biodegradability of the substance and its biological oxygen demand characteristics.

Registration of a new chemical substance in the United States and Japan requires similar comprehensive sets of data, although there are some differences. Obtaining all the data for a full registration can be time-consuming and costly.

In 1989 it cost approximately \$150,000 and took about a year to register a new substance in Europe.

In order to expedite the launch of a new chemical and allow further time to complete the toxicological package for full registration, a "limited announcement" is normally used. This requires only parts of the full toxicological packages, usually acute toxicity and Ames test. Consequently, it is less expensive (\$20,000) and quicker (90 days) than full registration. However, only 1 t or less of the chemical per year is allowed to be sold in the EEC.

The outcome of these toxicological tests determines the fate of the chemical. If the chemical is a potential human carcinogen it is abandoned. If it is nontoxic in all the tests then it is free to be sold as a commercial product. If the chemical gives inconclusive results at the first stage of screening, for example, an Ames positive response, then one of two courses of action is taken: either further *in vivo* testing is authorized or the chemical is abandoned. Which course of action is taken depends on the likely economic viability of the chemical. For a technically excellent product with a high profit margin aiming at a large market, further expensive animal testing would be justified. However, a chemical with a borderline technical profile and/or aimed at a smaller, more uncertain market would probably be abandoned.

10.2. Environmental Concerns. Dyes, because they are intensely colored, present special problems in effluent discharge; even a very small amount is noticeable. However, the effect is more aesthetically displeasing rather than hazardous, eg, red dyes discharged into rivers and oceans. Of more concern is the discharge of toxic heavy metals such as mercury and chromium.

Effluents from both dye works and dyehouses are treated both before leaving the plant, eg, neutralization of acidic and alkaline liquors and heavy metal removal, and in municipal sewage works. Various treatments are used (34).

Biological treatment is the most common and most widespread technique used in effluent treatment, having been employed for over 140 years. There are two types of treatment, aerobic and anaerobic. The aerobic system needs air (oxygen) in order for the bacteria to perform the degradation process on the activated sludge, whereas anaerobic bacteria operate in the absence of air. Activated sludge usually removes only a moderate amount (10–20%) of the color. Red reactive dyes are a problem because they are very visible, and losses in manufacturing are especially high.

Removal of color by adsorption using activated carbon is also employed. Activated carbon is very good at removing low levels of soluble chemicals, including dyes. Its main drawback is its limited capacity. Consequently, activated carbon is best for removing color from dilute effluent (see CARBON, ACTIVATED CARBON).

Chemical treatment of the effluent with a flocculating agent is the most robust and generally most efficient way to remove color. The process involves adding a flocculating agent, such as ferric ion (Fe^{3+}) or aluminium (Al^{3+}), to the effluent. This induces flocculation. A coagulant may also be added to assist the process. The final product is a concentrated sludge that is easy to dispose of.

Chemical oxidation is a more recent method of effluent treatment, especially chemical effluent. This procedure uses strong oxidizing agents like ozone, hydrogen peroxide, chlorine, and potassium permanganate in order to force degradation of even some of the more resilient organic molecules. It has even been demonstrated that ozone, for example, is quite capable of decolorizing most textile effluents. The use of ozone in combination with uv light has also shown some added potential in its ability to neutralize many common pesticides. For the moment, these treatments remain very expensive and of limited size, though they may have some promise in the future.

Further strategies being implemented to minimize dye and related chemical effluent include designing more environmentally friendly chemicals, more efficient (higher yielding) manufacturing processes, and more effective dyes, eg, reactive dyes having higher fixation (see DYES, ENVIRONMENTAL CHEMISTRY).

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Patents

These contain most of the dyes and intermediates on chemistry and technology, but in general are more difficult to access than books and journals. Dyes are classified under Section E2 of Derwents World Patents Index Classification.

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