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Aromatic amines: use in azo dye chemistry

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1. ABSTRACT

This chapter provides an overview of the chemical structures and properties of aromatic amines and their role in the development and utility of azo dyes. Approaches to the design of environmentally benign alternatives to genotoxic primary aromatic amines, as azo dye precursors, are included.

2. INTRODUCTION

2.1. Structural nature

Azo dyes comprise about two-thirds of all synthetic dyes, making them by far the most widely used and structurally diverse class of organic dyes in commerce (1). They are used to color synthetic and natural textile fibers, plastics, leather, hair, paper, waxes, petroleum, and certain food, drug and cosmetic products (2). Structurally, they contain one or more –N=N– moieties built into a conjugated system (Figure 1). As the generic structure suggests, essential precursors of azo dyes are aromatic amines.

Aromatic amines used in azo dye formation are 4n plus 2 pi-electron systems in which a primary ($–NH_2$), secondary (–NHR), or tertiary ($–NR_2$) amino group is attached to a carbocyclic or heterocyclic ring. Their structures are manifold and include amino-substituted benzenes, naphthalenes, and heterocycles such as those shown in Figure 2 and Figure 3. As the representative structures suggest, aromatic amines can be hydrophobic or hydrophilic, simple or complex, and vary widely in electronic (donor/acceptor) properties. In the sections that follow, it will be shown that their structural nature determines the types of substrates that have affinity for the resultant azo dyes and the technical properties of the resulting substrates.

2.2. Formation

While aromatic amines used in azo dye chemistry can be formed in a wide variety of ways, reduction of the corresponding nitro compounds is by far the most often used method (3). Commonly used methods include: 1)

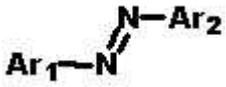


Figure 1. Generic structure for azo dyes, where Ar_1 and Ar_2 are aromatic systems.

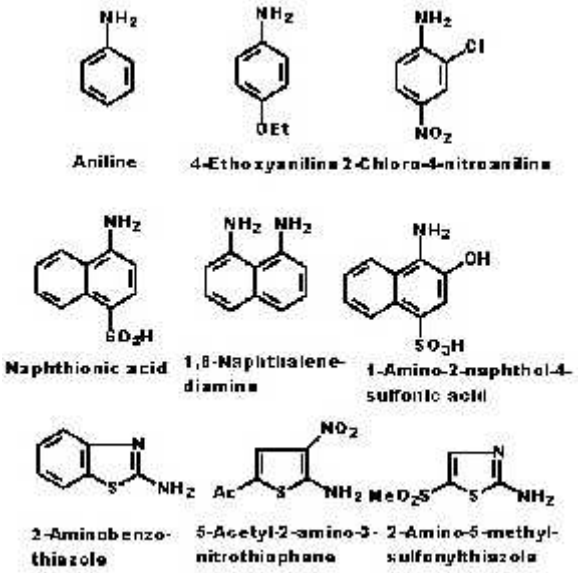


Figure 2. Examples of benzene-, naphthalene-, and heterocyclic-based primary aromatic amines used in azo dye synthesis.

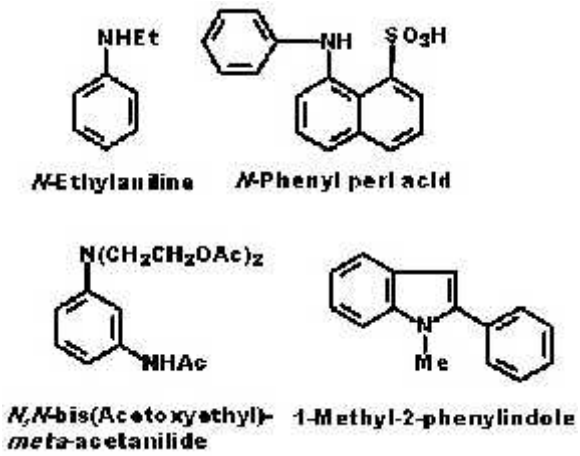


Figure 3. Examples of secondary and tertiary aromatic amines suitable for azo dye synthesis.

reduction with iron (Fe) in the presence of acids such as HCl, H_2SO_4, or HOAc; *2*) reduction with the mono- or di-sodium salts of H_2S (i.e. NaSH or Na_2S); 3) reduction with Zn and acid or alkali; and 4) reduction with hydrosulfite (e.g. $Na_2S_2O_4$). The first method is important in the manufacture of the simplest aromatic amine (i.e. aniline) and the more complex tetra-substituted naphthalene shown in Figure 4 (cf. **3**). Fe/HCl is used for its economy and its reducing power, as two nitro groups in the same molecule can be reduced by this agent (Figure 4, fourth entry). For milder reducing conditions, NaSH is often used. This permits partial reduction of dinitro compounds, as illustrated in Figure 5. This also allows one to obtain the monoamine and diamine from a common precursor (4). The ease with which azo bonds are cleaved in the presence of reducing agents makes azo dyes suitable precursors for aromatic amines. This means that azo dye **5** (Figure 6) is readily converted to 5-amino-salicylic acid (**6**) (5), a compound that is difficult to form efficiently in other ways.

In a relatively old and well studied process, nitrobenzenes are converted to diaminobiphenyls (benzidines; **8**) via the two steps shown in Figure 7 (6). Step 1 involves the use of Zn plus alkali to give hydrazo compounds **7,** which are not isolated, and step 2 is acid-induced rearrangement to give the target diamines.

Two other very important methods for forming aromatic amines used in azo dye synthesis involve the Bucherer reaction (Figure 8) and nucleophilic replacement of labile substituents such as halogens (cf. Figure 9). As indicated through three examples, the Bucherer reaction is important in the naphthalene system, providing a way to convert hydroxyl-substituted naphthalenes (naphthols) to naphthylamines such as naphthionic acid, gamma acid, and Tobias acid (7). The first example shows that this reaction utilizes hot ammonium bisulfite solution to effect the conversion of Neville and Winther's acid to naphthionic acid. The formation of gamma acid demonstrates that the Bucherer reaction exhibits selectivity when the starting compound has hydroxyl groups in alpha and beta positions. In this regard, the beta-hydroxyl group is replaced by an $-NH_2$ group. In the third example, the formation of Tobias acid is an important reaction because it permits the use of a noncarcinogenic "form" of beta-naphthylamine in azo dye synthesis, with the sulfonic acid group removed in a later step (8). The Figure 9 examples of aromatic amine formation illustrate the ability of nitro groups to activate replacement of chloro groups (9). The first example shows that this can be a selective replacement when only one of the chloro groups is adjacent to a nitro group (cf. X = Cl). The third example shows that complex amines, in this case a disulfonated naphthylamine, can be used to replace a labile chloro group. Halogens such as fluorine and bromine can also be used in these reactions but the required nitroaryl halides are less economical.

3. PROPERTIES

3.1.Chemical

With regard to chemical properties, aromatic amines are organic bases, as they 1) accept a proton (H^+) from an acid and 2) donate a pair of electrons to form a bond at an electron-deficient center (10). This means that they are also nucleophiles, which opens the door to a variety of azo dye precursors as illustrated in Figure 10. The first example depicts an important reaction leading to disperse dyes for hydrophobic polymers such as poly(ethylene terephthalate), whereas the second and third

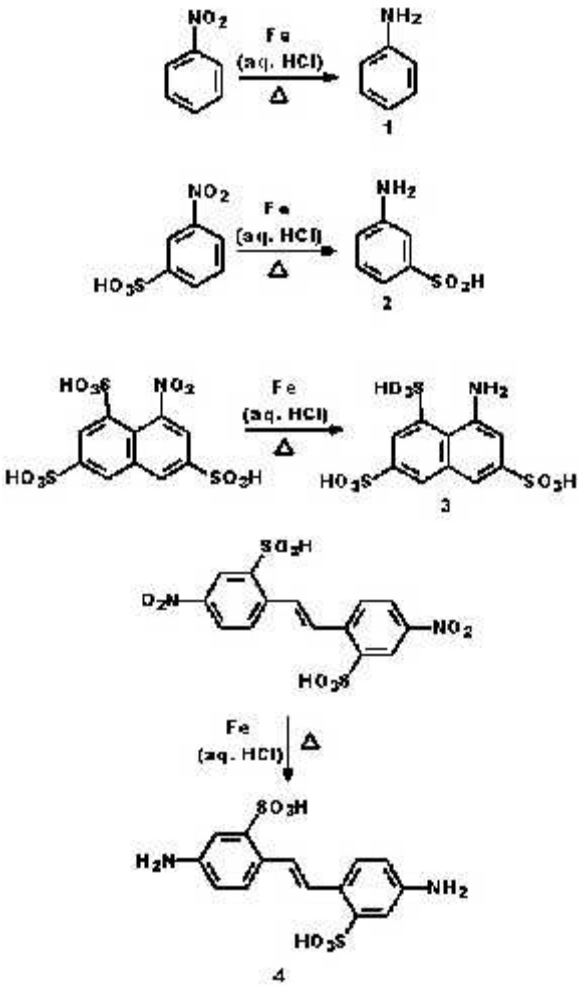


Figure 4. Aromatic amine formation via reductions using Fe/aq. HCl.

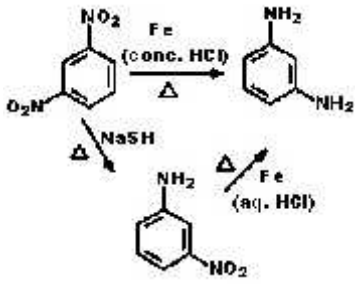


Figure 5. Aromatic amine formation from *meta*-dinitrobenzene.

are important in the synthesis of reactive and acid dyes for cellulosic and polyamide polymers, respectively.

In addition to reactions at the nitrogen atom, aromatic amines undergo reactions with electrophilic species at ring carbon atoms, owing to activation of *ortho*- and *para*-positions via delocalization of the lone pair on nitrogen. This is illustrated in Figure 11 which shows the PiSystem (11) calculated distribution of electrons over the atoms of the pi-system. The relative sizes of the circles indicate the sites more susceptible to electrophilic attack. In the case of aniline and its acetylated derivative, electrophilic attack on the aromatic rings is predicted to occur at *ortho*- and *para*-positions. Therefore, acetaniline can be converted to 2-chloro-4-nitroaniline according to the sequence shown in Figure 12. In this synthesis, it is important to acylate the amino group before nitration to prevent its protonation. Otherwise the resultant $-NH_3^+$ group would direct the incoming nitro group to the *meta*-position. The acetyl (Ac) group is removed following chlorination (12), upon heating the chlorinated intermediate in aqueous acid (H_3O^+) or alkali in the final step of the reaction sequence.

The reactivity of aromatic amines at the N-atom is reduced upon adding electron-withdrawing (ring deactivating) groups to the ring, especially in *ortho* and *para* positions, due to delocalization of the lone pair electrons (see Figure 13). Similarly, 2-amino heterocycles such as those shown in Figure 2 are weakly basic amines, requiring strong acids for dissolution (13). There will be more on these ring systems later.

3.2. Azo dye formation

Regarding azo dye chemistry, the most important reaction of aromatic amines is diazotization, which is the conversion of an $-NH_2$ group to an $-N_2^+$ (diazo) group (14). This process typically employs a mineral acid (e.g. HCl, H_2SO_4) and sodium nitrite ($NaNO_2$), as depicted in step 1 of Figure 14. In turn, the diazo group reacts with electron-rich aromatic compounds to produce azo dyes. Step 2 of this sequence is known as diazo coupling and the compound that combines with the diazo compound is called a coupler or coupling component.

Aromatic amines are used as diazo components and coupling components. While diazo components are always primary amines ($Ar\text{-}NH_2$), coupling components can be primary, secondary (Ar-NHR) or tertiary ($Ar\text{-}NR_1R_2$) amines (15), where R = alkyl or aryl groups and R_1 and R_2 can be the same or different. Diazo components include aryl monoamines (e.g. anilines, naphthylamines) and diamines. The examples in Figure 15 show that suitable diamines contain a pair of $-NH_2$ groups on the same ring (e.g. 1,4-naphthylenediamine and *meta*-phenylenediamine), on attached rings (e.g. benzidines), or on rings separated by a spacer group (e.g. 4,4'-diaminostilbenes). Aryl diamines undergo diazotization to give compounds having two diazo groups (16) and, subsequently, two azo groups following diazo coupling (cf. Figure 16). When R = H, the dye obtained is the long used pH indicator Congo Red, also known as C.I Direct Red 28, the first direct dye for cotton fibers (17). This synthesis also illustrates the use of primary aryl amines as a diazo component in step 1 and a coupling component in step 2.

Azo dye formation can be characterized using the shorthand notations known as Winther symbols (Table 1), in which a combination of letters and arrows are used (18).

Table 1. Winther symbols used to describe azo dye formation

Symbol	Representation
A	A diazotizable amine
E	A coupling component that reacts once
D	A bis-diazotizable diamine
M	A 1^{o} amine that can couple and be diazotized
Z	A coupling component that can react twice

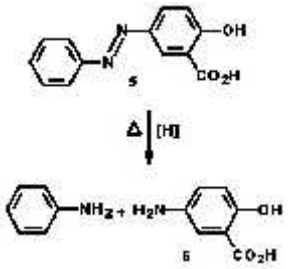


Figure 6. Aromatic amine formation via reduction using hydrosulfite.

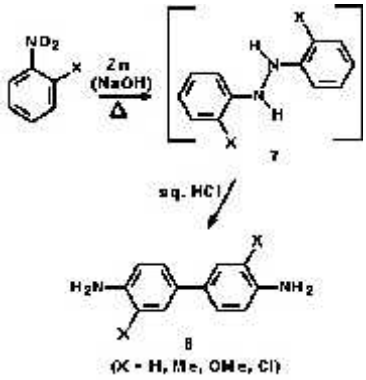


Figure 7. Aromatic amine formation via reduction using Zn/NaOH and subsequent acid treatment.

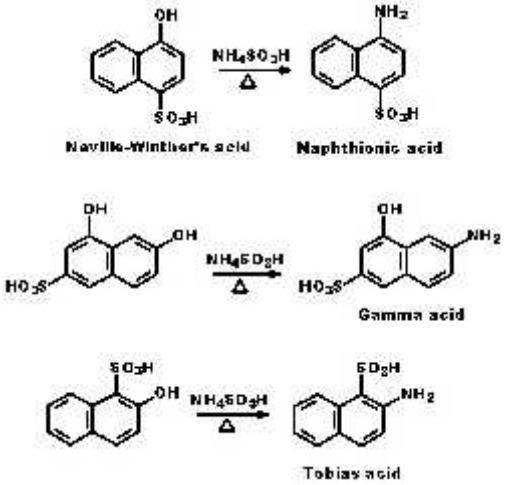


Figure 8. Aromatic amine formation via the Bucherer reaction.

With Winther symbols in mind, CI Acid Orange 7 (Figure 14) can be described as arising from an A to E synthesis, in which diazotized sulfanilic acid is combined with beta-naphthol, a coupling component that reacts once. Similarly, the Figure 16 dyes are formed by a synthesis in which a bis-diazotized diamine (D) reacts on both ends with a coupler (E; naphthionic acid) that reacts once. While the end groups are the same in this case, they need not be. When different couplers are used, the synthesis is described as a D to E_1 and E_2. The two other methods for forming bisazo dyes are A to M to E synthesis (Figure 17) and A_1 to Z and then A_2 to the same Z, where group A can be the same or different (Figure 18).

Figure 17 shows the retrosynthetic pathway associated with C.I. Direct Red 254. The two-step process indicates that the target dye is derived from coupling the intermediate monoazo dye with J-acid (E), which was first formed by coupling sulfanilic acid (A) with aniline (M). The target dye structure includes dashed lines to indicate the connection points required for assembling the structure, thus illustrating that a careful inspection of an azo dye structure will reveal how it was formed. Figure 18 shows the components employed in the preparation of C.I. Acid Black 1. Unlike the previous route, this two-step process has a single coupler that forms an azo bond on each end. The dye synthesis not only utilizes different diazotized amines it also uses a coupler that is a naphthylamine on one end and a naphthol on the other end. Bisazo dye synthesis from aminonaphthols involves coupling *ortho* to the $-NH_2$ group first and then *ortho* to the –OH group because the first coupling deactivates the aromatic system towards electrophilic attack. The ability to ionize the –OH group using alkaline media makes the second coupling reaction effective. In a case such as this, numbers 1 and 2 are often used to indicate the order of the coupling steps.

Trisazo dyes include those obtained via an A to M to M to E and a D to E and Z and then A to the same Z process. An example of the former type is C.I. Direct Brown 202, which is derived from sulfanilic acid (A), aniline (M_1), 1,7-Cleve's acid (M_2), and phenol (Figure 19). The –OH group of the initial trisazo product is ethylated to give an ethoxyphenyl moiety (E), making the dye less sensitive to alkaline media induced color changes When still widely used, trisazo dye C.I. Direct Black 38 (Figure 20) was made from a series of reactions involving *meta*-phenylenediamine (E), benzidine (D), H-acid (Z), and aniline (A).

3.3. Genotoxicity

Since 1972, IARC has published periodic monographs pertaining to the genotoxicity of aromatic primary amines. It is clear from Volume 1 and related updates (19-22) that lipophilic amines, especially those bearing *ortho*-methyl or *ortho*-methoxy groups, often pose a carcinogenic risk to humans. Bearing in mind that azo dyes are susceptible to reductive cleavage to produce aromatic amines employed in their synthesis, azo dyes derived from a variety of carcinogenic amines have been banned from commerce (cf. Table 2 and Figure 21) (23-25). The diversity in the structure of banned amines indicates that carcinogenicity can arise when one or two aromatic rings are present and when two aromatic rings are fused (cf. **9**), connected to form a biphenyl moiety (cf. **10**

Table 2. Aryl amines associated with German Industrial Standard 55943 and EU Directive 2002/61/EC

Structure	Name
9	2-Naphthylamine
10	4-Aminodiphenyl
11	Benzidine
12	3,3'-Dichlorobenzidine
13	3,3'-Dimethylbenzidine
14	3,3'-Dimethoxybenzidine
15	4,4'-Diaminodiphenylmethane
16	3,3'-Dimethyl-4,4'diaminodiphenylmethane
17	4,4'-Methylene-bis-(2-chloroaniline)
18	4,4'-Oxydianiline
19	4,4'-Thiodianiline
20	4-Aminoazobenzene
21	4-Amino-2',3-dimethylazobenzene
22	2,4-Diaminotoluene
23	2,4-Diaminoanisole
24	4-Cresidine
25	2-Aminotoluene (*ortho*-toluidine)
26	4-Chloro-*ortho*-toluidine
27	2-Amino-4-nitrotoluene
28	2,4,5-Trimethylaniline
29	2-Methoxyaniline (*ortho*-anisidine)
30	4-Chloroaniline

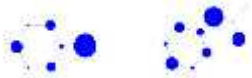


Figure 9. Aromatic amine formation via replacement of a labile chloro group.

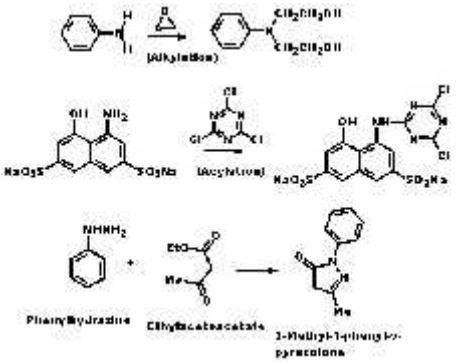


Figure 10. Nucleophilic reactions involving an aromatic amine, producing azo dye precursors.

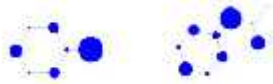


Figure 11. PiSystem calculated distribution of electrons over the pi-system of aniline (left) and acetanilide (right).

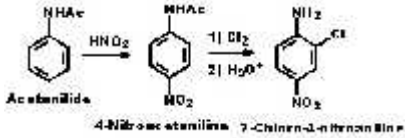


Figure 12. Electrophilic reactions (nitration, chlorination) typical of an aromatic amine.

14), or separated by a bridging group (cf. **15-21**). Banned benzene-based amines include substituted *meta*-phenylenediamines (**22-23**), *ortho*-anisidines **24** and **29**, and *ortho*-toluidines **25-28**. The common denominator is a primary aromatic amino group that is amenable to metabolic transformation to electrophilic species (e.g. nitrenium ion formation, Figure 22) (26).

In view of their importance in hair dyeing, *meta*-phenylenediamines **22-23** were the subject of studies aimed at removing mutagenicity from these prototypes. In those studies, it was shown that mutagenicity was reduced and eventually removed as the length of the alkyl chain was increased (cf. Figure 23) (27-28). Similar studies were conducted with *para*-phenylenediamines, with the same outcome. It was proposed that the presence of a bulky alkyl/alkoxy group *ortho* to one of the $-NH_2$ groups prevented oxidation to reactive *N*-species (29). The absence of mutagenicity in benzene-based diamines **31** and **32** led to an extension of this approach to carcinogenic benzidines (**11-14**). This work gave rise to the development of non-carcinogenic diamines **33** (Figure 24) and their use in azo dye and pigment formation (30-31).

Figure 25 shows additional diamines developed as potential benzidine alternatives. Though not used in commercial azo dye synthesis, tetramethylbenzidine **34** is noncarcinogenic (32). Its proposed use is in the detection of blood. Like diamines **33**, the $-NH_2$ groups are protected against oxidative metabolism. Proposed potential benzidine replacements lacking bulky *ortho* substituents include compounds **35-38** (33-38). Diamines **35** and **38** proved nonmutagenic and substrates for symmetrical bisazo dye synthesis. Due to differences in reactivity of the $-NH_2$ groups, diamines **36** and **37** provided the opportunity to make unsymmetrical bisazo dyes. As illustrated in Figure 26, the presence of an electron withdrawing group (e.g. C=O) gives the *para*-NH_2 group greater electron deficient character than the $-NH_2$ group on the opposite end. This causes the latter $-NH_2$ group to undergo faster reaction with HNO_2 in the diazotization step of azo dye formation. On the other hand, formation of bisdiazo intermediate **39** gives greater reactivity towards nucleophiles at the diazo group *para* to the C=O group (39) (Figure 27).

Benzidine analogs containing phenylene groups as spacer units have also been reported (cf. Figure 28). Results from mutagenicity testing showed that adding one phenylene moiety to the parent benzidine structure led to increased mutagenicity when n = 3 (40). At dose levels greater than 400 micrograms, DATP was toxic towards TA98, causing the mutagenicity level of benzidine (n = 2) to catch and later exceed that of DATP. On the other hand, DAQP (n = 4) was nonmutagenic (cf. Figure 29). This diamine has a high melting point (318 degrees C) giving it low solubility in most solvents, probably contributing to low bioavailability.

Dyes prepared from diamines **35-38** and **40-41** include **42-43** (Figure 30) and **45** (Figure 31). Dye **42** was prepared as an analog of C.I. Direct Black 38 and dye **43** was made as an analog C.I. Direct Blue 2. While, the

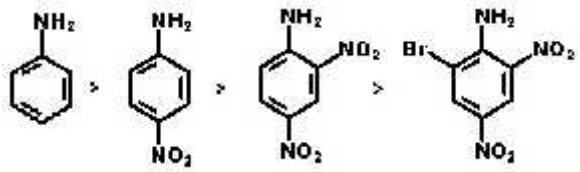


Figure 13. Relative order of reactivity at N-atom (basicity) of some anilines used in azo dye chemistry.

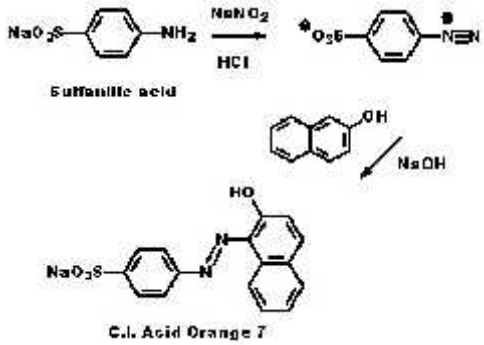


Figure 14. Two-step synthesis of an azo dye from an aromatic amine.

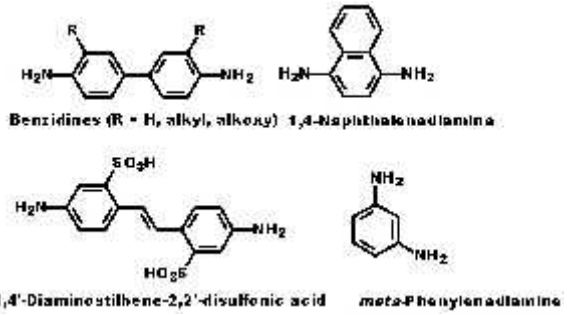


Figure 15. Examples of aryl diamines suitable for azo dye synthesis.

resultant dyes were non-mutagenic, their colors did not fully match those of the prototypes. Analogs of solvent dye **44**, a derivative of carcinogenic *ortho*-tolidine (**13**) were reported, an example of which is bisazo dye **45**. The use of diamine **37** (X = CO) provided a non-genotoxic alternatives to C.I. Direct Yellow 1 (cf. **46**), wherein the end coupler is salicylic acid. Diamino-dihydrophenophosphazines **38** were converted to non-mutagenic bisazo dyes **47**, which conferred blue colors to cotton fibers. Similarly, diamines **40**-**41** gave type **48** bisazo analogs of Congo Red, as illustrated in Figure 32. Despite these interesting and promising developments, it is not clear which of the alternative dyes have found their way into commerce. The higher costs of the new diamines and pressures felt by textile dye users to reduce production costs have made it difficult for dye manufacturers to broadly market new dyes. Thus new textile dye development, especially in the direct dyes area, is rare nowadays.

4. INFLUENCE ON DYE PROPERTIES

4.1. Color

Commercial azo dyes typically contain one or more electron-donating groups in conjugation with one or more electron-acceptor groups (cf. **49**). The stronger the push and pull of electrons, the more bathochromic the color. Thus, monoazo yellow to blue dyes have structures such as those shown in Figure 33. The structures illustrate that amino groups are stronger electron donors than a phenolic group, that tertiary amines are stronger donors than primary amines, and that aromatic amines containing multiple electron donors and acceptors produce violet and blue dyes. To circumvent the need for complex aromatic amines in order to produce a large bathochromic shift in monoazo dyes and to achieve the brightness associated with anthraquinone dyes, azo dyes based on heteroaromatic amines were developed. This development is illustrated in the comparison of structures for C.I. Disperse Red 167:1 and C.I. Disperse Red 156. The use of 2-aminobenzothiazole avoids the need for 2-chloro-4-nitroaniline and the strong electron donor in Red 167:1 to achieve a red color. Similarly, the use of 2-amino-5-nitrothiazole produces blue colors without the need for trisubstituted anilines employed in making C.I. Disperse Blue 79:1 and C.I. Disperse Blue 165. Further, the use of nitrothiophenes produces green colors not available by using aniline derivatives as the diazo component. See C.I. Disperse Green 9 (Figure 34). Similarly, the effects of varying the choice of heterocyclic amine on dye color are illustrated in Figure 35 for monoazo dyes **50**-**53**. These examples show that the benzoisothiazole system of **51** is more bathochromic than the benzothiazole system of **50** and that replacing the ring N-atom in the thiazole moiety in **52** with a C-nitro group to give thiophene **53** has a bathochomic effect (15, 41).

Monoazo dyes containing a naphthyl group in place of one of the phenyl group of azobenzene are characterized by orange to blue colors, as illustrated by the dye structures shown in Figure 36. Coupling sulfanilic acid to 2-naphthol gives C.I. Acid Orange 7 (lambda max = 483nm), which exists as a mixture of azo and hydrazone structures. Coupling naphthionic acid to 2-naphthol produces C.I. Acid Red 88 (lambda max = 505nm). Adding an –OH group *ortho* to the azo bond in naphthionic acid produces a structure that forms a metal complex with Cr(III), giving C.I. Acid Blue 161. Metal complexes of azo dyes are invaluable for stability to prolonged and repeated exposures to sunlight. The actual structures are often comprised of 2 dye molecules per metal ion and are known as 1:2 metal complexes (cf. **54**, Figure 37). Transition metals such as Cr, Co, Fe, and Cu are used in dye synthesis, with the former three metals used in acid dyes for nylon, wool, and leather and Cu used in metal complexed direct and reactive dyes for cotton. In the case of Cu, 1:1 or 2:1 complexes are formed.

The effects of coupler choice on dye color (lambda max in H_2O) are illustrated in dyes **55**-**61** (Figure 38), where it can be seen that reddish-orange to red colors are produced by coupling *meta*-nitroaniline to various sulfonated naphthols and naphthylamines. It is also clear that 1) coupling *ortho* to the amino group in gamma acid gives a higher lambda max than the analogous coupling with J-acid (cf. **55**/**56**), 2) replacing the $–NH_2$ group on naphthylamines with an –OH group produces a

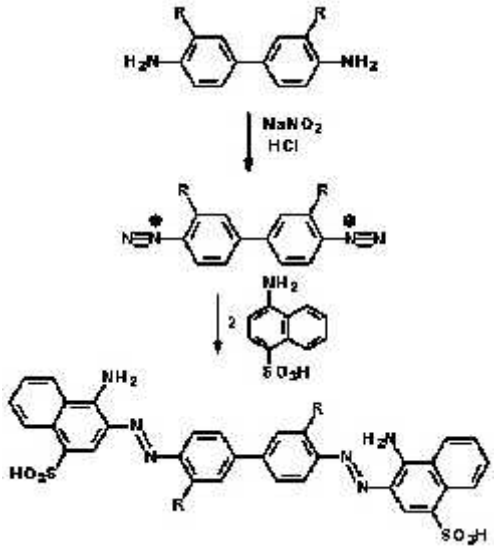


Figure 16. Diazotization and coupling reactions involving benzidine type diamines, where R = H, alkyl, alkoxy.

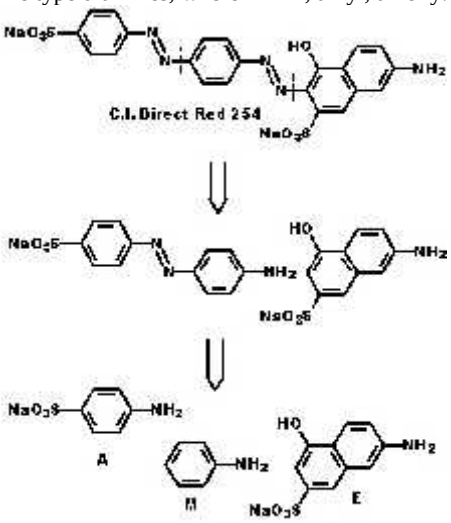


Figure 17. Retrosynthetic pathway for C.I. Direct Red 254, an A to M to E process.

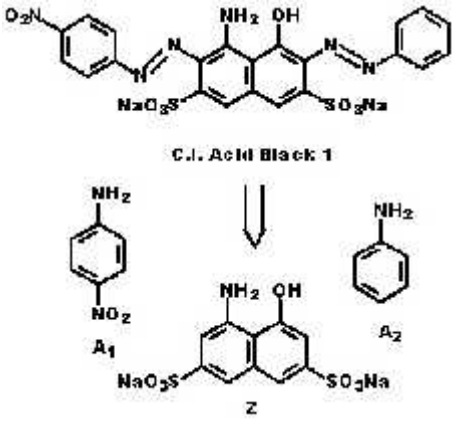


Figure 18. Retrosynthetic pathway for C.I. Acid Black 1, an A_1 to Z and A_2 to same Z process.

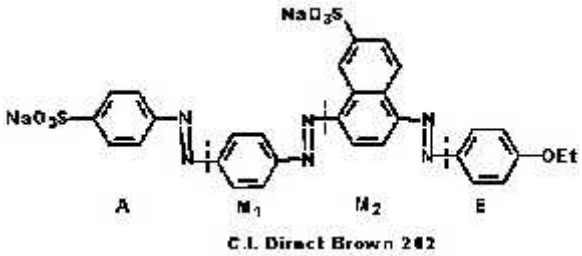


Figure 19. Structure and assembly points for C.I. Direct Brown 202, an A to M_1 to M_2 to E process.

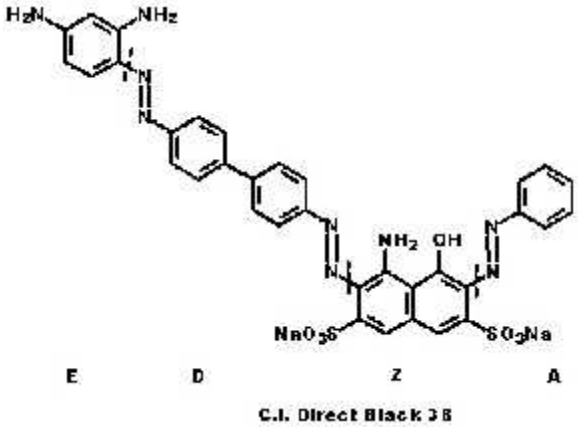


Figure 20. Structure and assembly points for C.I. Direct Black 38, a D to E and Z and A to same Z process.

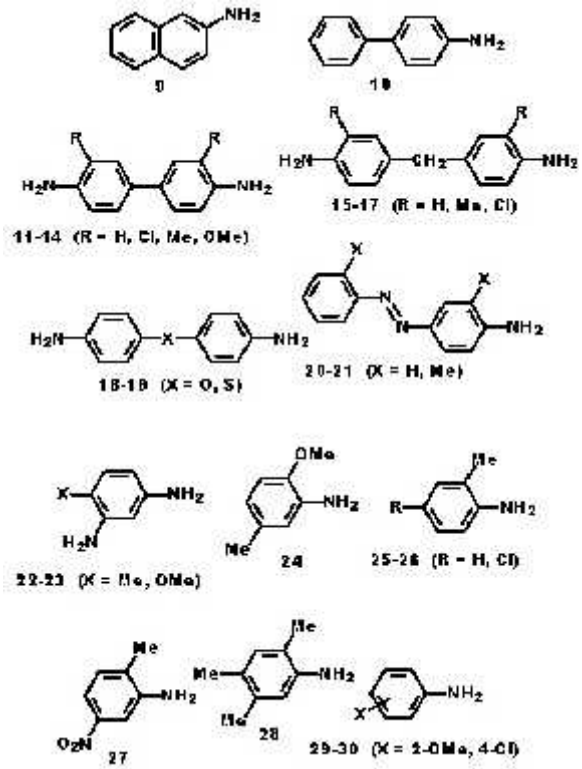


Figure 21. Structures of 22 aromatic amines restricted from use in commercial textile and related products.

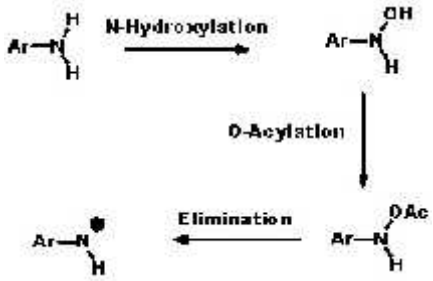


Figure 22. Metabolism of a primary aromatic amine to give an electrophilic species.

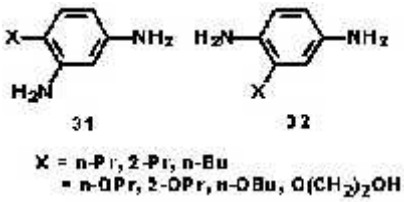


Figure 23. Structures of non-mutagenic *meta*- and *para*-phenylenediamines.

Figure 24. Structures of non-genotoxic benzidines.

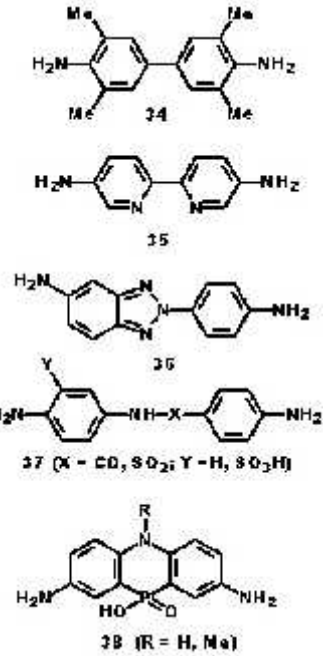


Figure 25. Additional diamines developed as potential benzidine replacements in azo dye synthesis.

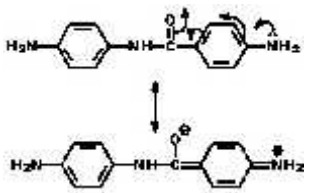


Figure 26. Resonance structures for type **37** diamine (X = C=O), showing difference in electronic properties of the $-NH_2$ groups.

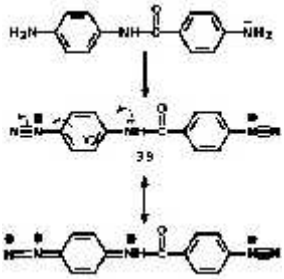


Figure 27. Resonance structures for bisdiazo intermediate **39**, showing difference in electronic properties of the $-N_2^+$ groups.

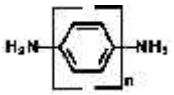


Figure 28. Phenylene homologs of benzidine.

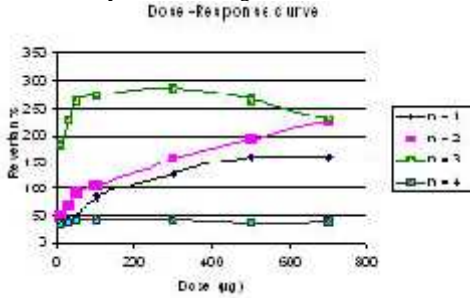


Figure 29. Mutagenicity data for diaminophenylenes in TA98 +S9.

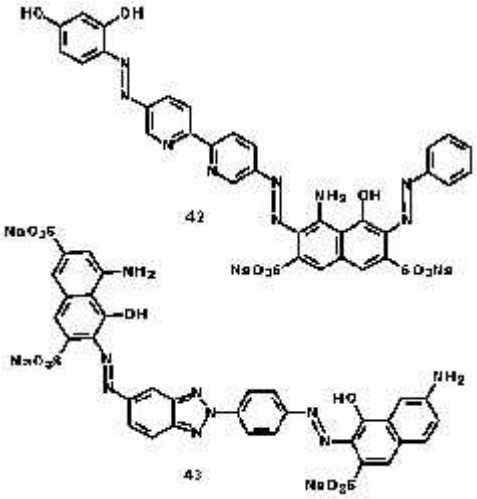


Figure 30. Nonmutagenic direct dyes derived from diamines **35**-**36**.

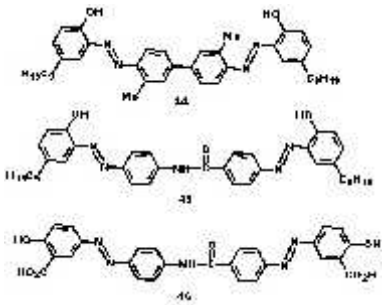


Figure 31. Genotoxic solvent dye **44** and related nongenotoxic disazo dyes **45**-**46**.

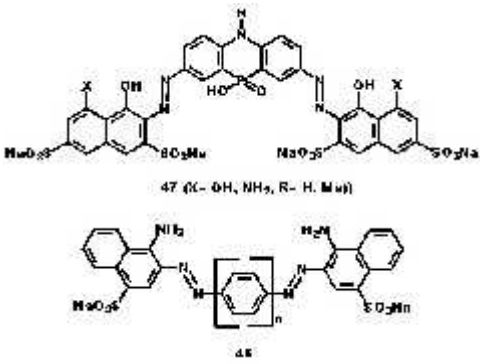


Figure 32. Novel disazo dyes (**47**-**48**) derived from diamines **38** and **41**.

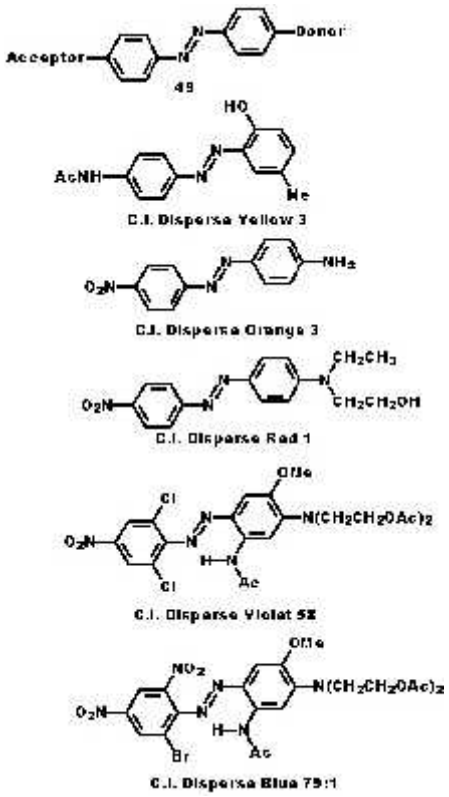


Figure 33. Dye structures illustrating the bathochromic effects of increasing push and pull of electrons on color.

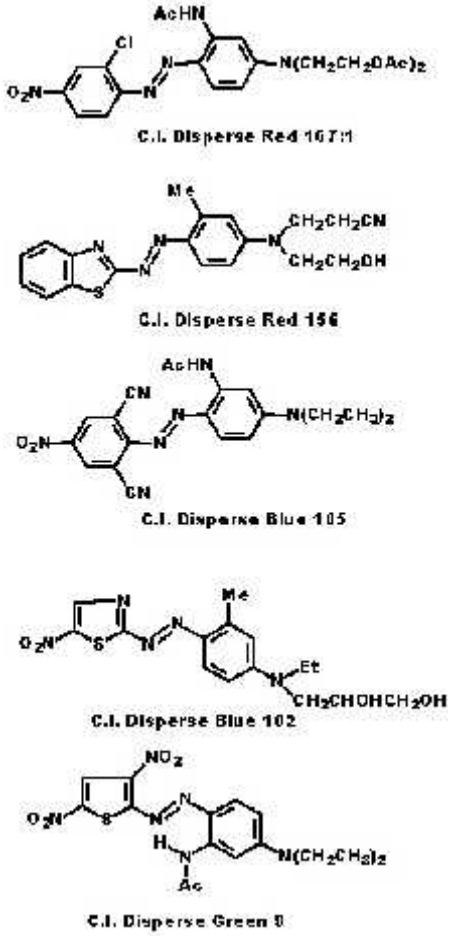


Figure 34. Dye structures illustrating colorants from using hetero-aromatic amines in lieu of benzene amines.

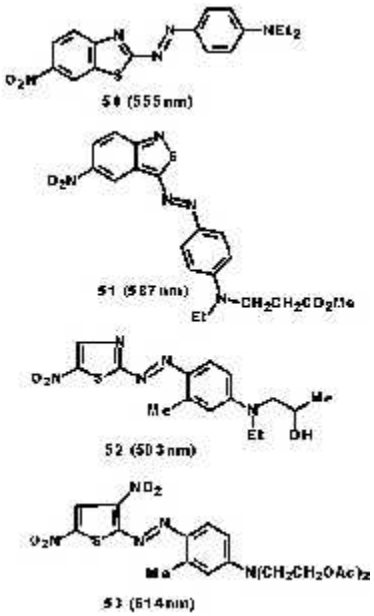


Figure 35. Dye structures illustrating the effects of varying hetero-aromatic amines on lambda max.

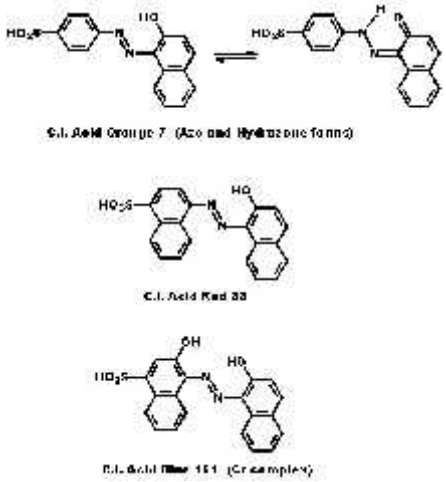


Figure 36. Dye structures illustrating the bathochromic effects of using naphthylamines in place of a phenylamine.

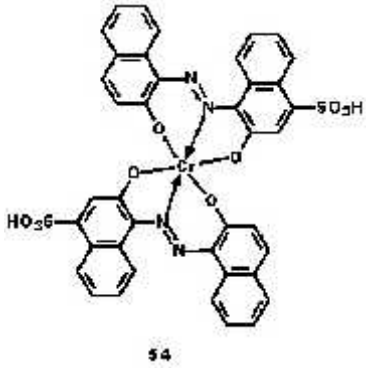


Figure 37. C.I. Acid Blue 193, a 1:2 Cr-complex dye.

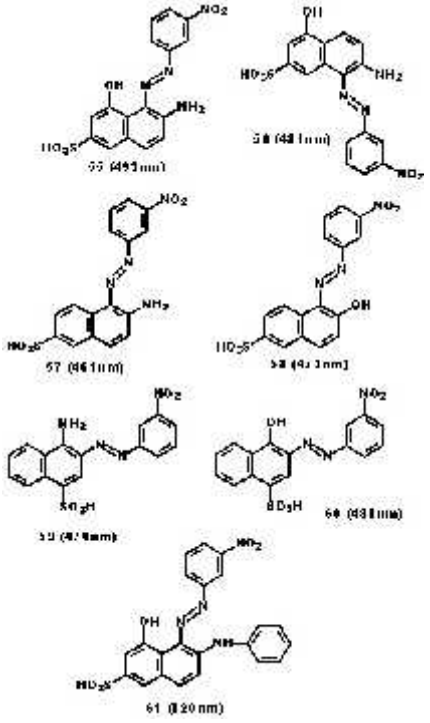


Figure 38. Illustration of effects of coupler choice on lambda max.

bathochromic effect (cf. **57**/**58** and **59**/**60**), and 3) attaching a phenyl group to the *N*-atom of gamma acid pushes the dye color well into the red region (cf. **61**). Unlike arylazo naphthols, arylazo naphthylamines do not exhibit azo-hydrazone tautomerism, which accounts for the lower lambda max values. Figure 39, the absorption spectrum of dye **55**, shows a single band rather than the pair of bands typical of tautomeric forms. However, the absorption band is somewhat broad, which is characteristic of dyes giving rather dull shades when applied to substrates such as textiles. The use of naphthalene-based couplers in monoazo dye formation can also produce bluish-red colors, as illustrated in dyes **62-65** (Figure 40) which employ the amino-dihydrophenophosphazine system (42).

Regarding bisazo dyes, yellow and orange dyes include **66** and **67** (Figure 41) which have an A to M to E structure, a phenolic end group, and employ two aromatic amines in their synthesis. Use of alpha-naphthylamine in place of aniline as the M-group in dye **66** causes a bathochromic shift and gives orange dye **68**. A further bathochromic shift is observed when the phenolic end group is replaced by a naphthol group (cf. dye **69**; Figure 42). In this case, 2-naphthol is used, giving rise to hydrazone form **70** and intramolecular H-bonding. The use of naphthylamines as center (M) and end (E) groups in bisazo dyes produces blue dyes such as **71** (Figure 43). In the case of D to E_1 and E_2 bisazo dyes, yellow to blue colors have been produced, examples of which are **43**-**48**.

Azo black dyes are often trisazo structures of types **72-75** (Figure 44 and Figure 45) (43) and direct dyes for cellulosic substrates. These dyes arise from coupling D to E and M followed by M to E (**72** and **73**) and A to M to M to E (**74** and **75**) syntheses involving four aromatic amines.

4.2. Coloration (dye-polymer affinity)

The design of azo dyes takes into consideration the substrate that is to undergo coloration. In this regard, dyes are designed to match the chemical nature of the substrate. This means, for instance, that hydrophilic dyes are required for hydrophilic fibers. The target properties are largely derived from the choice of aromatic amines used in azo dye synthesis. Although a myriad of substrates are amenable to coloration, they fall largely into two broad categories, viz. nonionic (hydrophilic or hydrophobic) and ionic (cationic or anionic) (44-45). Nonionic hydrophilic substrates include cellulosic polymers/fibers (**76**), nonionic hydrophobic substrates include polyesters (**77**), polyamides (**78**), and polyolefins (**79**), and anionic substrates include proteins (**80**) and acrylics (**81**), as shown in Figure 46 and Figure 47.

Cellulosic substrates such as cotton undergo coloration by water soluble (sulfonated) azo dyes in two principle ways – covalent bond formation or intermolecular interactions (e.g. H-bonding). These dye–polymer fixation mechanisms are illustrated in Figure 48 and Figure 49. H-bonding can involve the -OH groups on the cellulose chain and electron pairs on hydroxyl, amino, or azo groups in the dye structure (cf. Figure 48). Reactive dyes such as the

dichlorotriazines undergo replacement of labile groups to form covalent bonds with cellulose (cf. Figure 49).

Hydrophobic polymers such as polyethylene terephthalate (PET) form solid-solid solutions when the matrix takes on hydrophobic disperse dyes shown in Figure 33, Figure 34, and Figure 35, as illustrated in Figure 50. Hydrophobic interactions also occur on nylon when dyes containing long alkyl chains are employed, as shown in Figure 51. This leads to high resistance to dye removal during wet processing steps such as milling (46).

The presence of anionic or cationic groups within the backbone of polyacrylonitrile and protein fibers (wool, silk) permit coloration using dyes having the opposite charge (cf. Figure 52). Therefore, cationic azo dyes such as **82** can be applied to fibers bearing an anionic group. Similarly acid dye **83** (cf. Figure 53), direct dyes (e.g. **72-75**; Figure 44 and Figure 45), and the Figure 49 reactive dye can all be applied to wool fibers, owing to the presence of one or more anionic groups in their structure. Upon dye dissolution in water, the $-SO_3H$ groups are ionized to $-SO_3^-$ groups. Although type **83** azo dyes (Figure 53) do not bear a sulfonic acid group, they still form ionic bonds to cationic fibers, owing to the present of a net negative charge arising from the attachment of four negatively charged O-atoms to the Co(III) ion. These dyes can be applied to cationic fibers such as wool at neutral pH.

4.3. Technical Properties

4.3.1. Wet fastness

The ability of dyed substrates, especially fabric and printed paper, to hold onto adsorbed dyes when brought into contact with water is an important property. As would be anticipated, high wet fastness is essential for dyed textiles that are frequently washed and for printed paper to maintain readability following inadvertent spills. This applies especially to cotton because the fibers are swollen to a high degree by water, opening pores in amorphous regions where dyes are located. As mentioned previously, azo dyes for cellulosic fibers are derived from sulfonated aromatic amines (cf. Figure 54 and Figure 55), which facilitates their removal by water but is necessary for dye-fiber affinity. To circumvent this dichotomy, direct dyes are modified following their application to cotton or reactive dyes are used.

Direct dye modifications are illustrated in Figure 56 and Figure 57. The simplest method involves treatment of the dyed fabric with a cationic fixative to reduce dye solubility in water by "masking" the sulfonic acid groups with a hydrophobic moiety thus minimizing interactions with water. The more complicated method involves diazotization of aromatic $-NH_2$ groups in the dye structure followed by coupling with 2-naphthol in the presence of alkali. This enlarges the dye molecules, making desorption more difficult and simultaneously lowers water solubility. Note that the Figure 57 enlargement process increases the number of azo groups from 3 to 5. Since increasing the number of azo groups is often accompanied by a color change, it is essential for the new color to be the one sought by the dyer. Due to difficulties with precise fabric shade reproducibility using this approach, this method is often restricted to black colors, where slight shade variations are often less objectionable.

Reactive dyes are the culmination of a long-sought way to produce bright wet fast colors on cotton leisure wear. Many have 1 or more azo groups in their chromogen and are typified by the 3 structures in Figure 58. The earliest include DCT dyes such as Reactive Yellow 86, which can be made by condensing cyanuric chloride with the corresponding arylaminoazo precursor (**84**, Figure 59). Note that precursor **84** is derived from 4,6-diamino-1,3-benzenedisulfonic acid (cf. Figure 55). C.I. Reactive Red 198 and Reactive Black 5 employ 1-amino-4-(2-sulfooxyethylsulfonyl)benzene in their synthesis and have two groups capable of forming a covalent bond with cellulose. This feature enhances the dyeing efficiency of reactive dyes whether the 2 reactive groups are different (e.g. Reactive Red 198, Figure 58) or the same (e.g. Reactive Black 5). Reactive Red 198 is made from MCT precursor **85** (Figure 60) which requires aryl amines H acid and metanilic acid.

A small family of Procion T reactive dyes was developed to explore the benefits of dyes that could be applied to cotton in the absence of alkali (47). It was envisioned that such dyes would be far less prone to hydrolysis during the dyeing process and thus more efficient colorants. These dyes contain 1 or 2 phosphonic acid ($-PO_3H_2$) groups and are derived from aromatic amines such as **86** and **87**. In turn, amine **86** has been converted to coupler **88**, a precursor for monoazo dye synthesis (Figure 61). Examples of Procion T monoazo reactive dyes are **89** and **90**. Both dyes form phosphonate type ester linkages, as illustrated in Figure 62 for the dicyandiamide (DCA)-mediated bonding of **90** to cellulose.

A special family of aromatic amines was developed to provide high wet fastness in dyes for ink-jet printing on paper. These amines include compounds **91-93** (Figure 63), containing carboxylic acid groups ($-CO_2H$) in lieu of sulfonic acid groups ($-SO_3H$). This variation provides dyes having high water solubility in inks, particularly when the $-CO_2H$ groups are converted to ammonium carboxylate (CO_2NH_4) groups, but low solubility following regeneration of the less water soluble free-acid forms upon contact of the ink with paper (Figure 64). This property, known as differential solubility (48-49), is characteristic of dyes **94-95** and provided an approach to solving the problem of poor wet fastness in the initial ink jet dye prototypes such C.I. Food Black 2 (Figure 65).

4.3.2. Light fastness

The choice of aromatic amines used in azo dye synthesis is essential to getting high dye light fastness (photostability), a property needed in azo dyes experiencing repeated and prolonged exposure to sunlight - especially its UV component. Aromatic amine derivatives often used to produce lightfast azo dyes include compounds **96-102** (Figure 66). Diazotization of aromatic amine **96** followed by coupling with tertiary amine **97** produces dye **103** (C.I.

Figure 39. Absorption spectrum of dye **55** in H_2O.

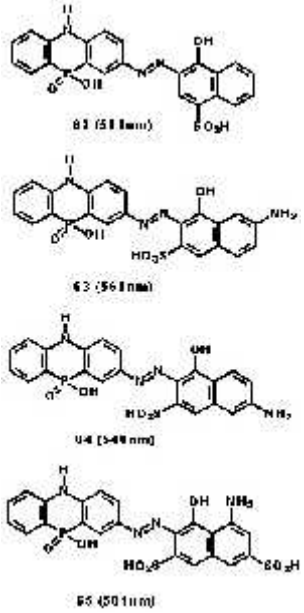
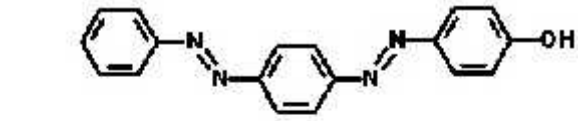
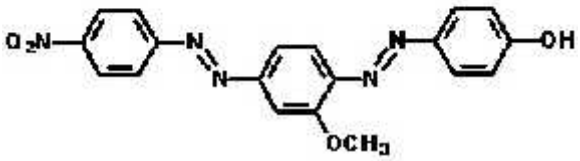


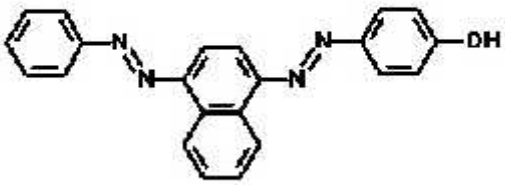
Figure 40. Monoazo dihydrophenophosphazine dyes.



66 (C.I. Disperse Yellow 23)



67 (C.I. Disperse Orange 29)



68 (C.I. Disperse Orange 13)

Figure 41. Representative bisazo disperse dyes.

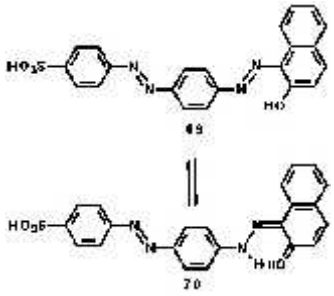


Figure 42. C.I. Acid Red 151 tautomeric structures.

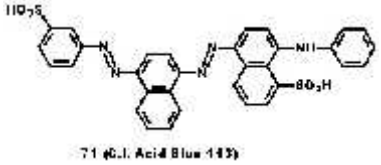
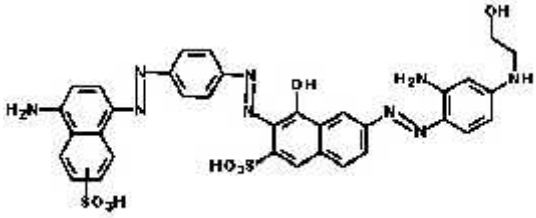


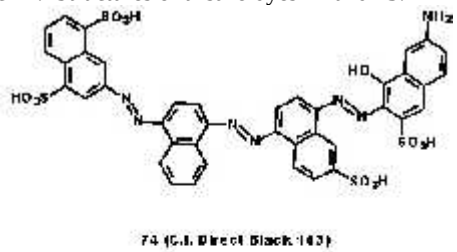
Figure 43. An A to M to E bisazo dye.



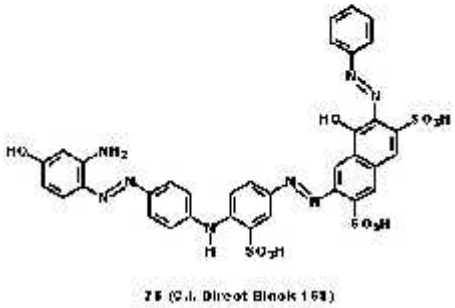
72 (C.I. Direct Black 2)

73 (C.I. Direct Black 164)

Figure 44. Structures of trisazo dyes **72** and **73**.



74 (C.I. Direct Black 163)



75 (C.I. Direct Black 168)

Figure 45. Structures of trisazo dyes **74** and **75**.

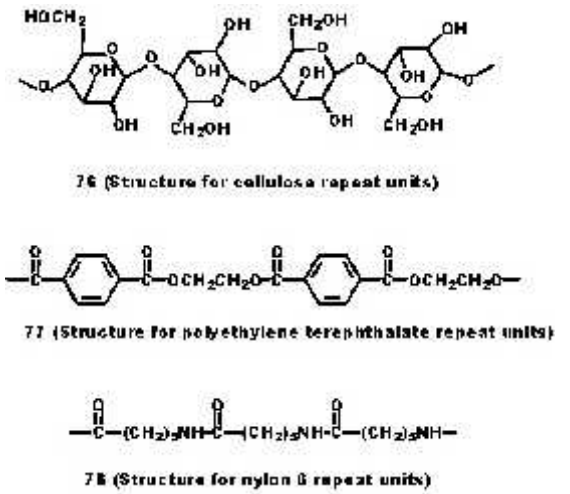


Figure 46. Nonionic polymers comprising fibers used in textile dyeing.

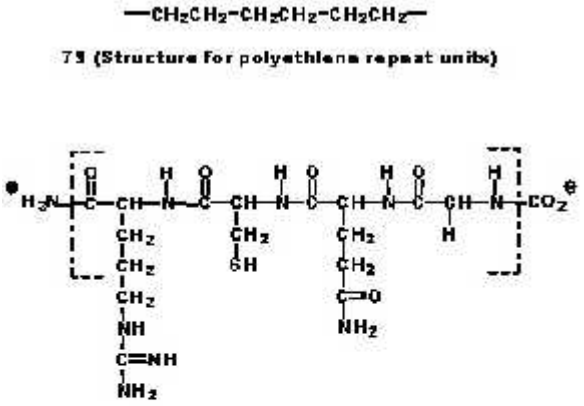


Figure 47. Ionic polymers comprising fibers used in textile dyeing.

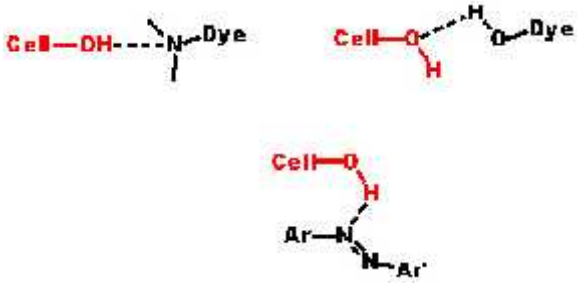


Figure 48. Azo direct dye fixation to a cellulosic substrate via H-bonding.

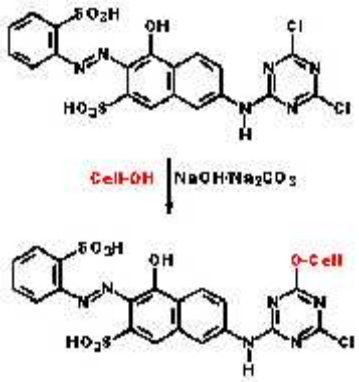


Figure 49. Azo reactive dye fixation to a cellulosic substrate via covalent bond formation.

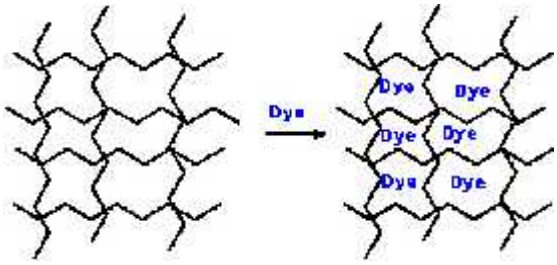


Figure 50. Hydrophobic azo dye fixation on PET via a solid-solid solution.

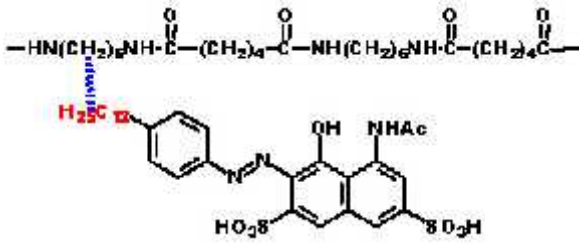


Figure 51. Azo dye fixation to nylon 66 via a hydrophobic interaction.

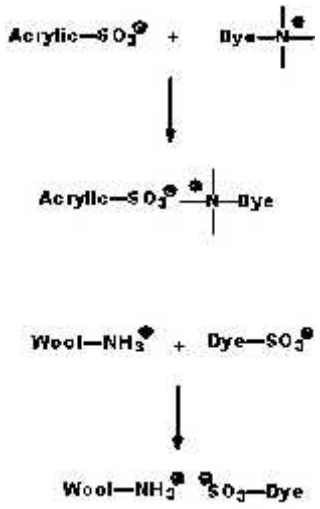


Figure 52. Azo dye fixation to anionic (top) and cationic (bottom) substrates via ionic bond formation.

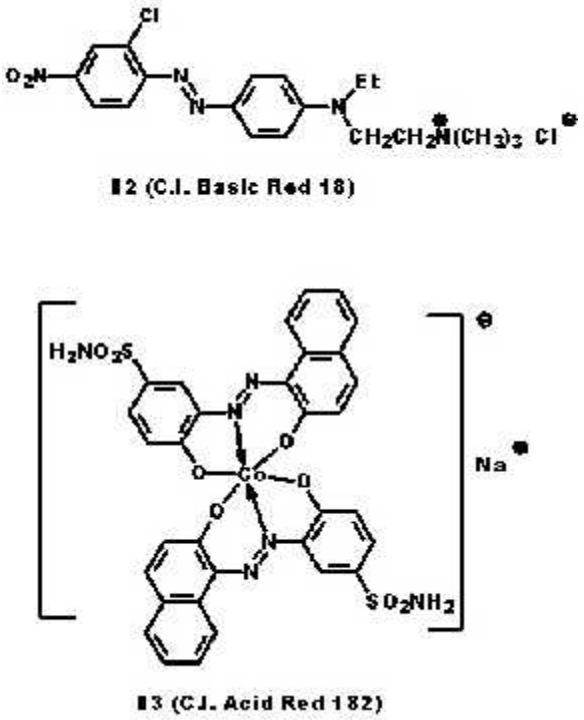


Figure 53. Examples of dyes forming ionic bonds during coloration.

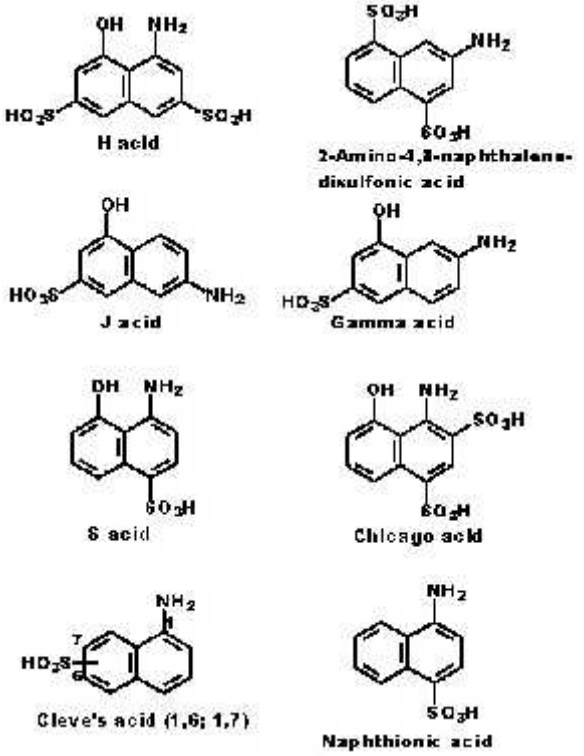


Figure 54. Representative naphthylamines used in dyes for cellulosic fibers for textiles and paper.

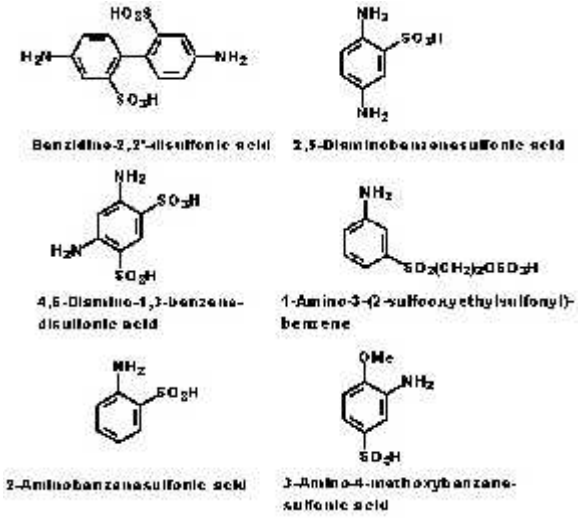


Figure 55. Representative phenylamines used in dyes for cellulosic fibers for textiles and paper.

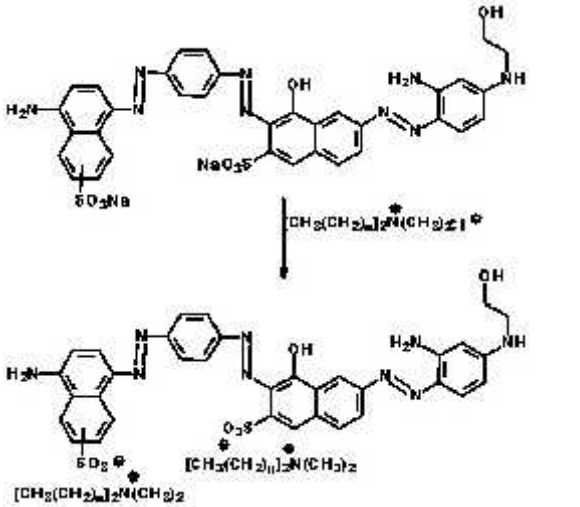


Figure 56. Use of a cationic fixative to enhance direct dye wet fastness on cotton.

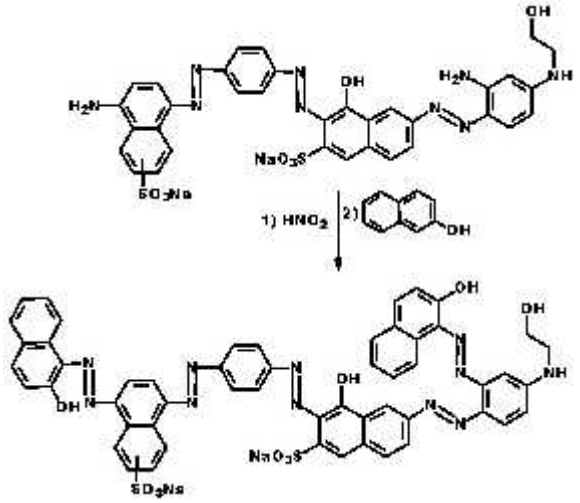


Figure 57. Chemical development of an NH_2-substituted direct dye to enhance wet fastness on cotton.

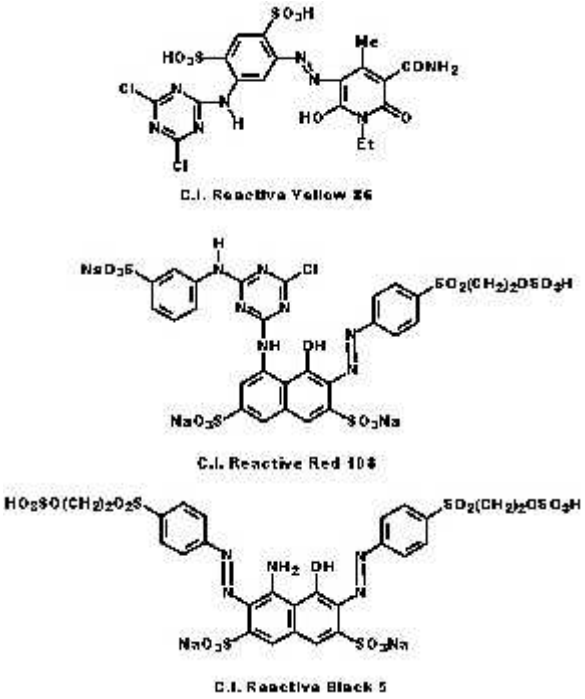


Figure 58. Representative reactive dyes developed for high wet fastness on cotton.

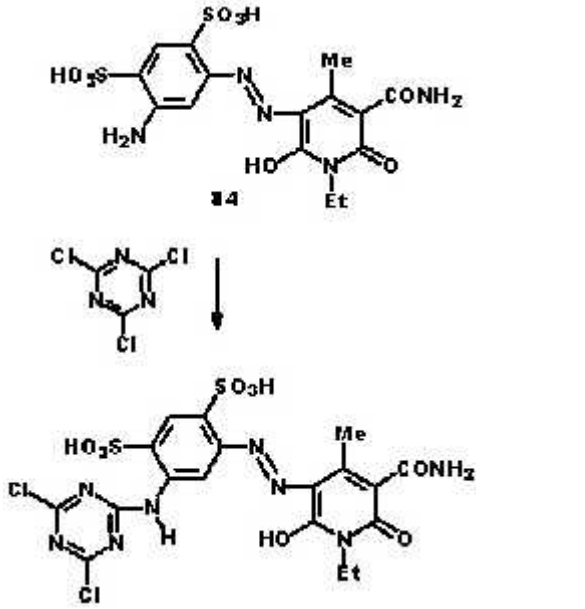


Figure 59. Reactive dye formation from an arylaminoazo precursor.

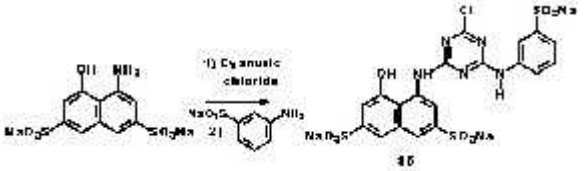


Figure 60. Formation of C.I. Reactive Red 198 precursor.

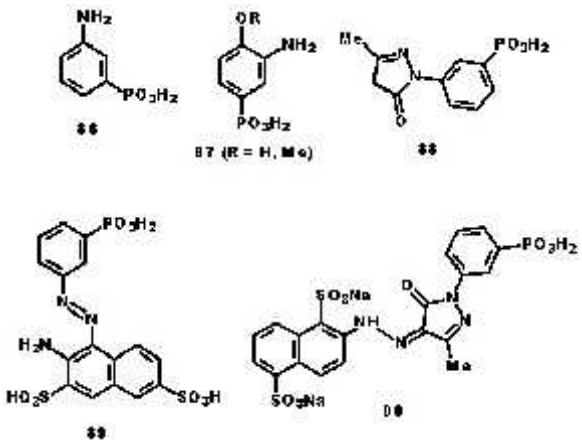


Figure 61. Procion T dye precursors (**86**-**88**) and dyes (**89**-**90**).

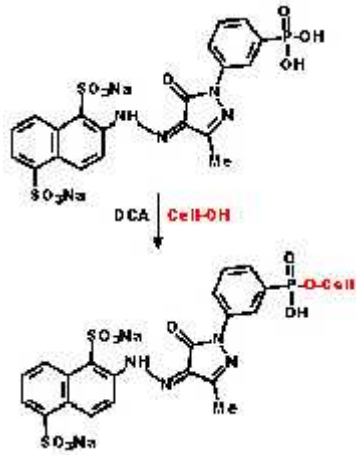


Figure 62. Phosphonate bond formation involving cellulose and Procion T dye **90**.

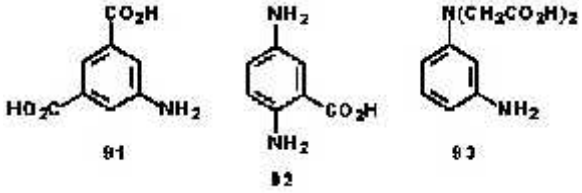


Figure 63. Aromatic amine precursors for ink-jet dyes.

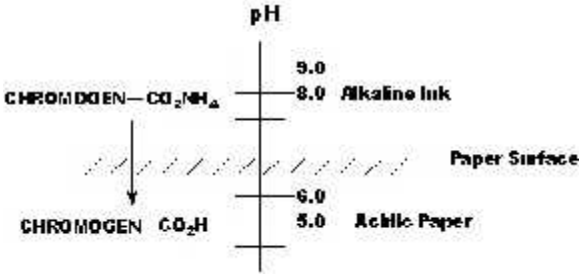


Figure 64. Conversion of a soluble ink-jet dye to its less soluble form on paper.

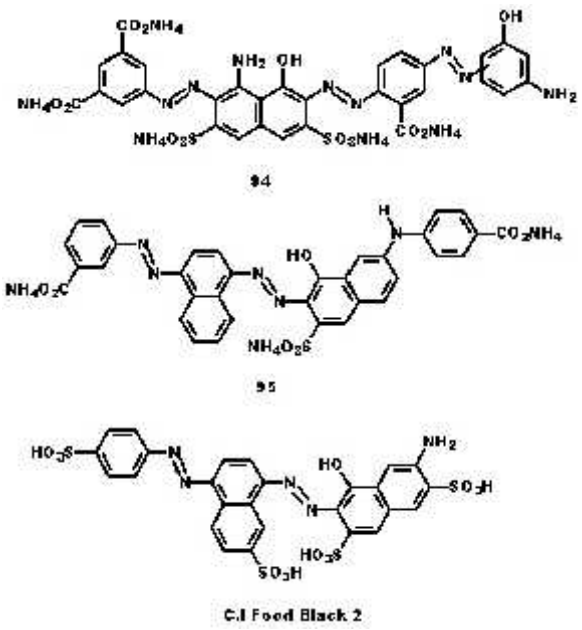


Figure 65. Black dyes for ink-jet printing on paper.

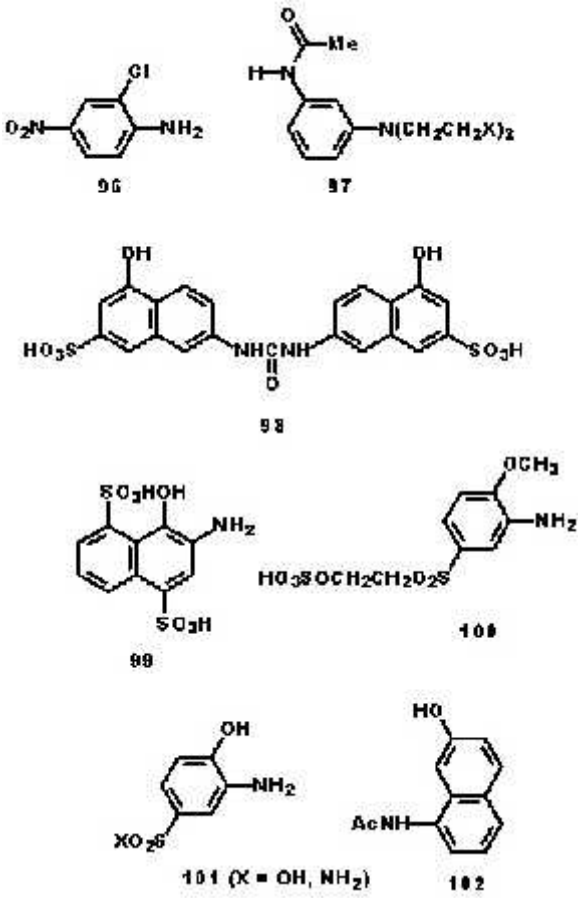


Figure 66. Aromatic amines used in lightfast azo dye synthesis.

Disperse Red 167:1; where X = OAc), one of a small number of light fast monoazo dyes for polyester used in automobile interiors. Use of amines **96** and **97** introduces 3 stabilizing features: 1) an acetamido group (NHAc) *ortho* to the azo bond in dye **103** leads to intra-molecular hydrogen bonding between the amide proton ("a") and the azo bond; 2) stability to bond "b", a site known to undergo cleavage by UV light, is achieved via delocalization of the lone pair electrons on the tertiary amino group (Figure 67). Delocalization is facilitated by the pull of electrons by the nitro group, to give structure **104**; 3) stability to pendant side chain "c" is achieved by acetylation of –OH groups often present in **97**. UV light cleavage of -$N(CH_2CH_2OH)_2$ groups to give an -$NH(CH_2CH_2OH)$ moiety causes an objectionable color shift. Type **97** couplers containing side chains with X = CN also stabilize the pendant side chains, enhancing light fastness in azo dyes for polyester.

Aromatic amine derivatives such as **98** (J acid urea) can be formed by condensing J acid (Figure 17) with phosgene ($COCl_2$). Compound **98** affords light fast azo direct dyes following coupling with 3-amino-4-hydroxybenzene sulfonic acid to give bisazo dye **105** and subsequent reaction with $CuSO_4$ to give 2:1 copper complex **106**. Metal complex formation takes advantage of hydroxyl groups in the *ortho*, *ortho'*-positions adjacent to the azo bonds (Figure 68). Similarly, aromatic amines **99** and **100** afford light fast reactive dyes **107-108** (Figure 69). Regarding dye **108**, the actual light fast dye is **109**, the formation of which requires cleaving the *ortho*-methoxy group in route to metal complex formation (50).

Aromatic amine **101** and acetylated aminonaphthol **102** are precursors for a light fast bisazo acid dye for polyamide and protein substrates. The target dye (cf. **110**; Figure 70) illustrates that a metal other than Cu is employed for these substrates. Light fastness in metal complexed azo dyes takes advantage of empty d-orbitals in the transition metals. In this regard, electrons associated with the azo bond can be deposited into these orbitals in the excited state, a phenomenon known as back-bonding (51).

4.3.3. Ozone fastness

The design of water soluble dyes for printing ink applications takes into consideration the stability of the target dyes to ozone, in view of the low levels of this oxidant produced by certain office copiers. *ortho*-Substituted anilines (**111**) have been used to generate dyes in which the conjugated system is protected against ozone attack (52). In this regard, it was reported that stability to ozone degradation for type **112** dyes (Figure 71) decreases according to the following substituents: 2-NO_2 is greater than 2-C_4F_9 is greater than 2-Br is greater than 2-CF_3 is greater than H is greater than 2-CH_3. While the electron-withdrawing effects of trifluoromethyl and nonafluorobutyl groups are comparable, it seems that the size (bulk) of the latter group affords greater resistance to ozone degradation.

Ozone fast dyes for printing inks (e.g. C.I. Direct Yellow 86) have been obtained using monoazo dye **115** as a precursor. This dye is formed by coupling disulfonated

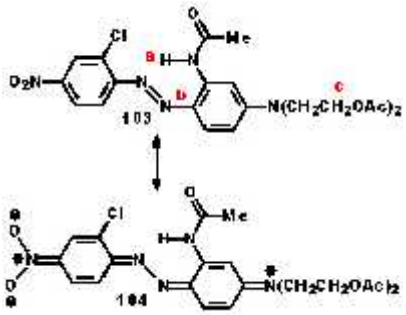


Figure 67. Stabilizing features in C.I. Disperse Red 167:1.

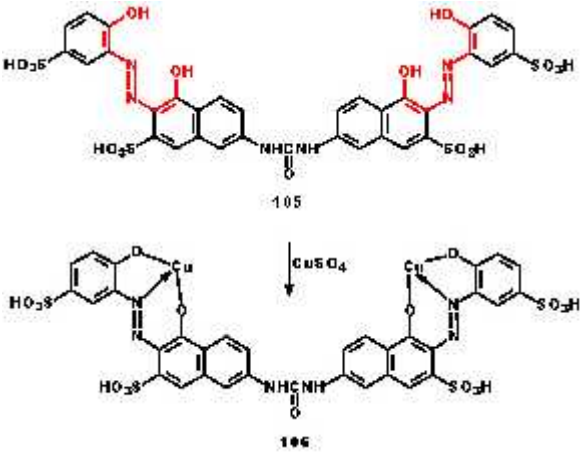


Figure 68. Metal complex formation involving a bisazo direct dye.

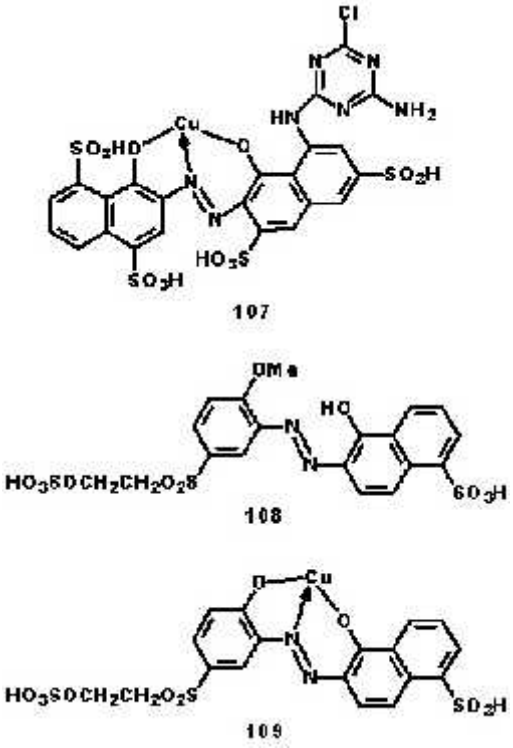


Figure 69. Examples of lightfast Cu-complexed reactive dyes.

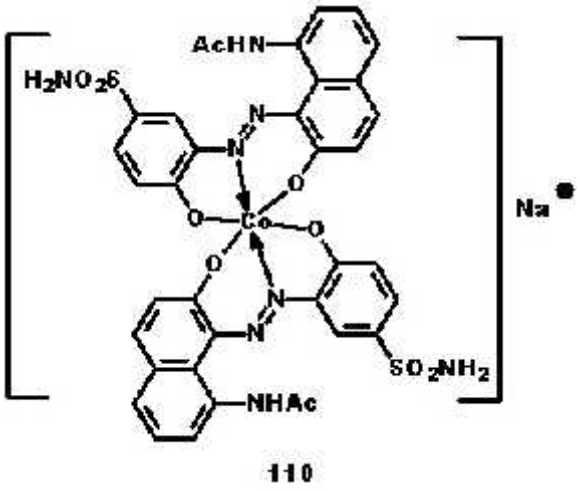


Figure 70. Example of a lightfast Co-complexed acid dye.

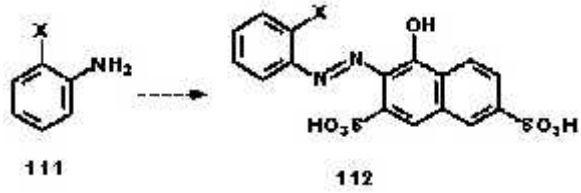


Figure 71. Arylamines (**111**) used in assessing azo dye ozone fastness on paper.

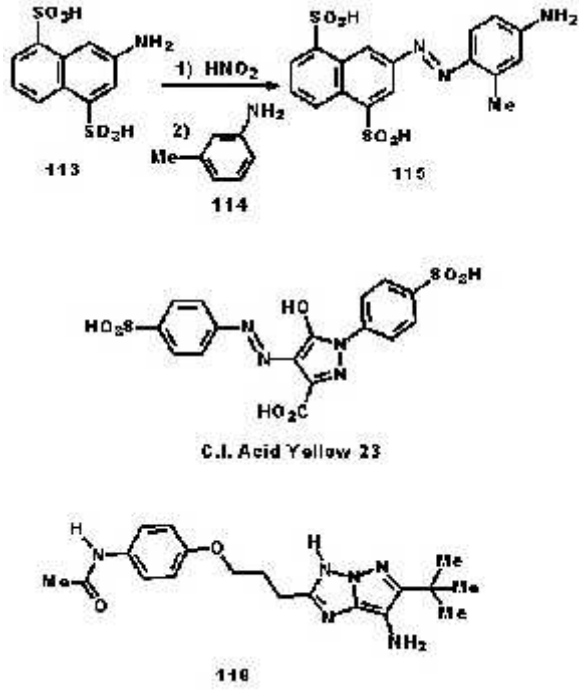


Figure 72. Additional compounds considered for ozone resistant azo dyes for paper.

naphthylamine **113** to *meta*-toluidine (**114**). Similarly, coupling sulfanilic acid (cf. Figure 14) to *N*-phenylpyrazolones has afforded ozone fast monoazo acid dyes such as C.I. Acid Yellow 23. To produce dyes having both light and ozone fastness, mono dyes have been developed using complex heteroaromatic amines such as **116** (Figure 72). The resulting dyes were specifically designed for use on porous, fast drying ink jet substrates (53).

5. SUMMARY

Aromatic amines are essential precursors in the formation of azo dyes, the largest family of synthetic dyes in commerce today. They vary widely in structure and chemical and biological properties, opening the door to the design of dyes for most end uses requiring coloration. In addition, the judicious selection of aromatic amines allows the chemist to develop a target color for a specific substrate and with a specific set of properties.

While the genotoxicity of certain aromatic amines has led to a banning of specific ones in many parts of the world, it has been possible to design replacements. Thus, new azo dye development takes into the consideration genotoxicity of the aromatic amines used in dye manufacturing and those formed by reductive cleavage of target dyes.

The economy of most aromatic amines and the relative ease with which they are converted to azo dyes ensure their importance for generations to come. Few, if any, color chemists worldwide would argue against the proposition that no other class of organic compounds is more important in the field of dye chemistry.

6. ACKNOWLEDGEMENT

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Abbreviations: Ar: aryl; C.I.: Colour Index; DAQP: diamino quarterphenyl; DATP: diamino terphenyl; DCT: dichlorotriazine; HOAc: acetic acid; MCT: monochlorotriazine; NaSH: sodium hydrosulfide; Na_2S: sodium sulfide; nm: nanometers

Key Words: Aromatic amines, azo dyes, diazo coupling, light fastness, genotoxicity, molecular design, basicity, synthesis, Review

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