Disperse Dyes: A Dye Chemist's Perspective

By Max A. Weaver, retired from Eastman Kodak Co., Kingsport, Tenn.

The history of disperse dyes is inseparable from the development of the new man-made, hydrophobic fibers that required the new dye class to be developed. When cellulose acetate, the first hydrophobic fiber, was developed in the 1920s, the existing hydrophilic dyes that had been used for the natural fibers were not suitable for dyeing the new material. Some limited success was achieved using some simple anilineazo dyes containing sulfomethyl groups that would hydrolyze in the dyebath to yield the free base under certain pH conditions. However, the disperse dye industry actually began when some British companies discovered that grinding water-insoluble dyes with surface active agents provided an aqueous colloidal dispersion when combined with water. For the next 25 years, the new dyes were simply called "acetate dyes." However, in the 1950s, new developing fibers such as polyamides, polyesters, triacetate, acrylics, and modacrylics resulted in the name change to "disperse dyes" in 1953, in view of the upcoming 2nd edition of the Colour Index in 1955.1

EASY DISPERSE DYE HISTORY

New Fibers

Although textile dye chemists made great advances in the 1950s by providing dyes for acetate with improved properties such as fastness to light, gas (oxides of nitrogen), washing, etc., the introduction of the new fibers brought even more stringent and different property requirements for disperse dyes. Polyesters, polyamides, and triacetate required higher dyeing temperatures than acetate, which necessitated using dyes with excellent hydrolytic stability over rather wide pH ranges. Polyester dyes relied on resistance to sublimation for fabric printing, ironing, heat-setting, etc. The dry heat Thermosol dyeing process required dyes with outstanding thermal stability and fastness to sublimation. Durable press finishes on polyester/cellulosic blends required dyes that would not change shade in the presence of various harsh resin catalysts, including acidic metal salts. Polyester/wool blends required dyes that gave little staining on wool or at least stains that could be removed.

The introduction of textured filaments polyesters, which found widespread use in apparel fabrics, required bright dyes with excellent pH and hydrolytic stability because of dyeing temperatures up to 275°F. Also, the preferred dyes showed little or no sensitivity in dye uptake to the heat history of the textured polyesters. Disperse dyes for polyamide carpet required excellent lightfastness, resistance to "Gulf Coast" fade, and stability to pH as high as 8-9 to decrease the staining of nylon with the oils in the jute backing.

Hydrophobic Fibers

Although not complete, the previous list of dye properties is enough to establish that much work was needed to satisfy the dye requirements for the developing fiber markets in the 1950s. Furthermore, by the 1960s, there was tremendous growth in the production of the new hydrophobic fibers (Table I). Growth in the secondary cellulose acetate fiber market had leveled off, but polyesters and polyamides showed strong growth with further growth predicted. These facts encouraged existing dye suppliers to increase research efforts and additional companies to enter the lucrative market.

Dye Producers

The late 1960s and 1970s brought the research and patenting efforts to new heights as shown by the U.S. patents on new disperse dyes and the increased number of dye producers. Between 1955 and 1971, the number of dye producers listed in the Colour Index more than doubled from 21 to 44. In the meantime, many major disperse dye producers built extra capacity in anticipation of continued rapid growth. By the 1980s, however, a number of factors initiated the demise of the U.S. textile dye industry including over capacity, increased number of imported dyes, decline in the overall U.S. textile business, increased costs for waste disposal, and implementation of TSCA and increased levels of toxicity testing for new dyes. New textile dye research in the United States had essentially stopped and textile dye chemists were an endangered species.

CHALLENGES IN DISPERSE DYE CHEMISTRY

Historical Research

Several challenges are immediately evident when creating new dyes with some improvement in properties that can be sold profitably in the marketplace. First, the dye chemist must be somewhat familiar with what has been done historically by other workers. At Eastman, this was done by obtaining copies of the U.S. patents (as well as some foreign patents) on disperse dyes that resulted in a patent library that began about 1930. They were then arranged into classes and subclasses for the most widely researched chromophores such as azo, anthraquinone, methine, o-nitroaniline, and a variety of miscellaneous chromophore classes. This allowed a quick review of known chemistry for specific structure types.

Second, the researcher had to become familiar with the dye chemistry that had been pursued within his/her present company. This was best accomplished by timely and detailed technical reports on dye preparation and properties.

Third, the disperse dye chemist needed to become knowledgeable about structure property relationships, particularly the all-important effect of structure on color.

Finally, since most dye companies benefited greatly by having patent protection on their new dyes, an understanding of the invention and patenting process was very helpful.

New Ideas

New ideas are the life's blood for the research, and the invention criteria are utility, novelty, and non-obviousness to one skilled in the art. My 44 years as a dye researcher led to the observation of several truths regarding invention. New ideas, and hence inventions, cannot be planned, scheduled, or directed. However, they can be encouraged and facilitated by an environment of free thought, hard work, and attention focused on the problems that need to be solved. Communication and discussion of ideas with fellow workers stimulate additional ideas. If not put to practice, even the

<table>
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<th>Fiber Production in Million of Pounds^a</th>
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<tr>
<td>Fiber</td>
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<tr>
<td>Acrylics and modacrylics</td>
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<td>Cellulose esters</td>
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<td>Polyamides</td>
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<td>Polypolyethylene</td>
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^a Private survey for Eastern Chemical Products Inc.

<table>
<thead>
<tr>
<th>Number of Textile Dyes Produced at Eastman through 1986</th>
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<tr>
<td>Color</td>
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<tr>
<td>Yellow</td>
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<tr>
<td>Orange</td>
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<td>Blue</td>
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<td>Brown</td>
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<tr>
<td>Black</td>
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<tr>
<td>No dye*</td>
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^a Represents colored compounds that decomposed during the dyeing process.
best ideas are useless. The dye chemist must develop the skill of defining the invention and recognizing what advantages are inherent when compared to the available prior art.

The information needed by the textile dye chemist must be generated empirically, not theoretically. This means that with the vast number of colored compounds provided by organic chemistry, the dye chemist can, and seems obligated to, prepare what seems to be an almost unlimited number of dyes for evaluation on various fabrics. To get some idea of the effort involved in doing research on disperse dyes, it is noted that work on acetate/disperse dyes started in 1934 at Eastman and continued until the dyes business was sold to Ciba-Geigy in 1986. Table II shows that over 54 years, more than 97,000 different dyes were prepared and evaluated. The "no dyes" category represents colored compounds that decomposed during the dyeing process.

Dye Evaluation
Not only did a large number of different dyes have to be prepared, but evaluation methods were needed for screening the dyes that were made in the laboratory in about 0.5-3.0 g quantities. The dyes were then dyed at two levels on cellulose acetate, polyesters, and polyanilines, allowing preliminary testing for basic properties such as fastness to light, sublimation, washing, etc. If a dye had attractive properties, larger scale and more complete property evaluations ensued. Small structural changes sometimes made significant differences in fastness and performance properties, and even different isomers and homologues usually showed some differences.

The early dye researchers at Eastman established a very convenient system for storing and retrieving the small dye samples that have been in place from about 1934 to the present. These samples have been very valuable for non-textile uses such as dyes for dye diffusion thermal transfer, imaging for photography, and thermally stable reactive dyes for copolymerization into polyesters and polyeurethanes.

Dye evaluation is complicated by the fact that dyes perform differently on different fibers. To discuss fastness of a dye, one must actually refer to the dye fiber substrate. For example, dyes that have outstanding fastness on cellulose acetate, and polyesters may have poor fastness on polyanilines and vice-versa. Historically, accelerated testing has been used to try to simulate actual long-term performance. Here the dye chemist becomes appreciative of associations such as AATCC for their interest in developing some standard test methods that are at least agreed upon by some experts in the field.

Summary of Structure Types
Historically, disperse dyes were selected mostly from anthraquinone, azo, methine, o-nitroaniline, quinophthalone, and a few miscellaneous classes. The azo class received by far the most attention, with anthraquinone being a strong second. Azo dyes have the advantage of color strength (high extinction coefficients), ease of manufacture, and economy. They also provide an entire gamut of colors. Even though the anthraquinones have lower color value and in general are more expensive, they continue to dominate certain parts of the market because of their brightness and combination of fastness and dyeing properties.

The most useful anthraquinone dyes have substituents in the alpha positions of the ring system and are usually derived from intermediates made by sulfonation of the anthraquinone ring in the presence of mercury salts, which provides alpha substitution as opposed to beta substitution. Mercury wastes have created pollution problems and proper disposal has added costs. Also, reactions for synthesizing anthraquinone dyes normally require an organic solvent that must be recovered or disposed of without harm to the environment. Many azo dyes are prepared in aqueous media with only acids and bases required.

The other three dye classes provided most of the yellow dyes, with the methine structures producing extremely bright yellow shades with excellent lightfastness. Some of the quinophthalones have become workhorse colors because of their excellent lightfastness and dyeing properties. Several o-nitroanilamines found their place with some of the best lightfastness available on polyester and cellulosic acetate. They are economical, but suffer from low extinction coefficients. Recent efforts to develop new chromophores for dyes and colorants have been summarized.

From 1965-1985, much research was directed toward azo dyes for polyester to replace the brilliant, but tinctorially weaker and more expensive anthraquinone dyes. Three important red anthraquinone dyes were the ancient C.I. Disperse Red 60 and two of its more sublimation fast derivatives, C.I. Disperse Red 92 and C.I. Disperse Red 159. The bright blue anthraquinones were best represented by neutral blues C.I. Disperse Blue 56 and C.I. Disperse Blue 73 as well as the bright, but very expensive turquoise C.I. Disperse Blue 60. The latter has the valuable property of flaring greener under incandescent light compared to daylight, in addition to having excellent lightfastness. The intense research effort to improve the brightness and lightfastness of the red and blue azo dyes has been documented.

Heterocyclic azo dyes derived from diazotizable heterocyclic amines have been widely investigated and reviewed because of their brightness and high extinction coefficients as well as the azo dyes derived from heterocyclic coupling components.

Dye Improvements
Another summary is not required since excellent reviews of disperse dye chemistry are available. However, it is desirable to give a couple of examples of improvement in the properties of disperse dyes that have resulted from research efforts of dye chemists. Many of the early orange to violet azo dyes were of the 4-aminoazobenzene structure (Fig. 1). This structure type has been one of the most widely investigated azo dye structures because of its versatility in color and availability of intermediates.

The entire color gamut from yellow to greenish-blue can be achieved by varying the substituents on Rings A and B and on the coupling nitrogen atom. The substituted anilines and the substituted aniline couplers are reasonably cheap, and the coupling reactions usually proceed in high yields. Several reviews relate to the effect of substituents on color in the 4-aminoazobenzene structure. Most of the early orange to bluish-red azo dyes for cellulose acetate and later for polyesters had this structure. The yellows were not reproduced since the dyes were phototropic unless in A
Fig. 2. Hydrogen bonding in chromogen.

-contained at least one group with strong electron-withdrawing properties that shifted from yellow to orange. The phototropism problem in yellow azo dyes was solved by replacing the substituted aniline couplers with heterocyclic couplers such as pyrazolones, indoles, pyridones, etc.

The nitro group in the 4-position on the azobenzene structure was usually desired because of the significant shift in the visible absorption band to longer wavelengths (bathochromic shift) and the accompanying increase in fastness to lightfastness on cellulose acetate and polyesters. Several observations on the effect of substituents on color in the 4-aminoazobenzene system were made. Negative groups in the 2-, 4-, and 6-positions in Ring A give the maximum bathochromic shift in the visible absorption band. Usually, three strongly electron-withdrawing groups are required to produce blue dyes. Also, the absorption maximum in the visible spectrum is dependent upon the basicity or electron density of the aniline coupling component. The presence of alkyl, cycloalkyl, and aryl groups for $R_1$ and $R_2$ provide bathochromic shifts as compared to $R_1$ and $R_2$ equal to hydrogen. Negative substituents on $R_1$ and $R_2$ give shifts in the absorption band (hypsochromic shift) to shorter wavelengths with usually an accompanying increase in fastness to lightfastness on cellulose acetate and polyesters.

Electron donating groups such as alkyl and alkoxy in Ring B, particularly in positions 2- and 5- provide bathochromic shifts, but unfortunately sometimes at the expense of lightfastness.

These effects may be explained theoretically by the valence-bond resonance approach (Fig. 1). In donor-acceptor chromogens such as 4-aminoazobenzenes, the absorption band may be accounted for by the different energy levels of structures I and II, with II being the higher energy level. Bringing the energy level of II closer to I moves electrons from the coupler nitrogen throughout the conjugated system to the electron-withdrawing group in Ring A at lower energy levels, thus requiring longer wavelength light. High-energy structures in II are stabilized by electron-withdrawing groups in Ring A and electron-donating groups in Ring B, which decreases the difference in energy between structures I and II.

**Effect of $m$-Acylamino Groups**

The discovery of an acylamino group in the 2-position of Ring B in the 4-aminoazobenzene dyes was one of the most significant advances in disperse azo dyes and was an area that received much attention by dye chemists from the 1960s to the 1980s (Fig. 2). The presence of the 2-acylamino group would be expected to cause little or no effect on color because it basically neither donates nor withdraws electrons according to the Hammett values. Surprisingly, however, the group gives a notable bathochromic shift, which has been used very advantageously by dye chemists. The effect may be explained by considering the stabilizing influence of the acidic hydrogen that provides hydrogen bonding and stabilization of the polarized state, thus lowering the energy required in the absorption of light and a shift to longer wavelengths.

This theory is supported by the fact that when the hydrogen in the acylamino group is replaced by an alkyl group, such as methyl, the group behaves exactly as a group having a Hammett value of about zero should have and shows little or no effect on color. Fortunately, for the polyester dye chemist, the bathochromic shift was usually accompanied by an increase in fastness to light, sublimation, and washing without significant loss in dyeing properties when compared to the same dyes where $R$ was hydrogen, alkyl, and alkoxy. Also, in some cases the visible absorption bands were narrower, which resulted in brighter dyes and sometimes an increase in extinction coefficient and color strength.

**C.I. Disperse Blue 79**

C.I. Disperse Blue 79, commercialized by Sandoz in the 1960s, was the first disperse dye containing a $m$-acetylamido group to achieve widespread use (Fig. 3). This dye and its homologue, where $R_2$ was methyl, were both suitable for producing navy and black shades for polyesters. The combination of the negative groups on the diazo component and the combination of the $2$-acetamido groups with the $5$-alkoxy groups provided the blue color. The $N,N$-bis(acetoxymethyl) and acetylamido groups added fastness to light, sublimation, and washing. This dye type quickly replaced the more expensive anthraquinone dyes of the day because of economy and properties for making navy and black shades.

This discovery spurred dye chemists to pursue azobenzene dyes containing acetylamino groups in order to produce a variety of new dyes in addition to the navy blue types. Fig. 4 shows some of the azo dyes for polyester that were commercialized in the late 1960s and 1970s. This type of dye resists shade changes when acid catalysts are used to cure durable press resins. These dyes illustrate how dye chemists have modified structures to improve fastness to sublimation that is dependent on the diffusion coefficients of the dye in the polymer substrate. Fastness to sublimation usually increases as the molecular mass and/or the polarity of the molecule increases. Thus, the large phenyl groups and the polar groups such as ester, ether, acylamino, and dicarbamimide all increase fastness to sublimation.

The effort to prepare bright blue 4-aminoazobenzene dyes was hindered in the early years because the highly negatively substituted anilines needed to produce bright blue shades were difficult to prepare and the dyes could not be prepared in high yields by direct diazotization and coupling because of the instability of the diazonium salts. This problem was overcome when Bayer dye chemists discovered that cyano groups could be introduced in the 2- and 5-positions by replacing halogens using metal cyanides. This displacement made these dyes economically attractive and produced bathochromic dyes with improved lightfastness and sublimation compared to the halogen-substituted intermediate dyes. From a commercial perspective, the dyes from 2-
bromo-4,6-dinitroaniline and 2,6-dibromo-4-nitroaniline received the most attention. Fig. 4 shows some of the bright blue to greenish blue dyes that were developed and sold to compete with the expensive C.I. Disperse Blue 73 and C.I. Disperse Blue 60 for some end uses. The advantage in color value of the azo dyes can be appreciated by noting that two of the azo dyes, C.I. Disperse Blue 337 and C.I. Disperse Blue 338, have extinction coefficients of 72,000 and 73,000, respectively, which is more than three times that of the typical blue anthraquinone dyes. The blue azo dyes had excellent fastness to light, sublimation, and washing, but still suffered in dyeing properties when compared to the anthraquinones for exhaust dyeing. To help the dyeability of C.I. Disperse Blue 165, the dyes from a mixture of N,N-diethyl- and N,N-din-propyl-m-acetamidoaniline couplers were utilized. 33 Disperse Blue 338 with the cyclized 1,2,3,4-tetrahydroquinoline coupler was a bright, greenish-blue dye capable of replacing Disperse Blue 60 in several combination shades with its ability to flare green under incandescent light when compared to daylight. Unfortunately, its use was limited to the thermofixation method of dyeing primarily.

**Heterocyclic Azo Dyes**

Intense research was done on heterocyclic azo dyes to replace anthraquinone dyes with brighter and more lightfast azo dyes (Fig. 5). This research in the 1960s and 1970s was spurred by the discovery of the brilliant blue azo dyes for cellulose acetate from 2-amino-5-nitrothiazole; for example, C.I. Disperse Blue 102, by J. B. Dickey, et al., at Eastman. 34 The dyes had only moderate lightfastness but were very strong and had excellent fastness to gas and very good dyeability. Also, some red azo dyes from certain substituted 2-aminoazothiazoles, such as 2-amino-6-methylsulfonylbenzothiazole-zole, were useful on both cellulose acetate and polyesters in the 1950s, but still lacked the brightness and lightfastness to compete with the bright red anthraquinones.

A few of the red-pink heterocyclic azo dyes that were commercialized in the 1970s had the necessary brightness, lightfastness, and color value to compete with some of the expensive anthraquinone red dyes are shown in Fig. 5. The dyes from 2-amino-5-ethylthio-1,3,4-thiadiazole diazo component and aniline couplers containing m-acylamino groups, such as acetamido, had a very desirable combination of brightness, lightfastness, and color value. C.I. Disperse Red 338 has an extinction coefficient of 55,000 (liter mol⁻¹ cm⁻¹), while most of the competitive anthraquinone dyes have extinction coefficients in the 13-14,000 range, thus indicating that the azo dyes were about four times as strong. 35 C.I. Disperse Red 340 had better lightfastness and leveling properties on polyamide carpet than the other two red dyes, making it a competitor for the expensive C.I. Disperse Red 55 and 55:1, which were widely used for polyamide carpet in the 1970s and 1980s. The green dye, C.I. Disperse Green 9, which was a product from the highly researched Gewald synthesis of substituted 2-aminothiophenes of the 1960s, had a unique shade and could be used as a green flaring dye under incandescent light for flare control. However, its use was limited because of moderate lightfastness. Some of these dyes offered the dyer and finisher tremendous savings without a compromise in properties while providing a reasonable return on investment for dye manufacturers.

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**Fig. 4. Typical 2'-acylamino substituted azobenzene dyes.**

**Fig. 5. Heterocyclic azo dyes.**
CONCLUSION

The golden years of the 1960s and 1970s for disperse dye research brought an array of new dye structures that were designed to meet a diversity of needs on a variety of hydrophobic fibers. Problems in the U.S. textile and dye businesses in the 1980s brought much textile dye research in the United States to a halt. Mock recently prepared a comprehensive review of the U.S. textile dye industry. During the 1990s, the larger European dye suppliers continued research at a decreased level, but have recently faced hard times due to extreme competition from low-cost dye producers continued research at a decreased level, but have recently faced hard times due to extreme competition from low-cost dye production in China, India, and the Pacific Rim countries. This has resulted in dye lines being streamlined with many companies undergoing mergers, consolidations, reorganizations, spin-offs, etc. Any observer in the field of textile dyes is aware that research has essentially stopped and the world’s dyes business continues to rest on the outstanding work of previous years.

Without any attempt to be prophetic, one must presume that things will not stay the same and free world trade will result in some sort of equalization. There may well be further innovation in textile fibers that cannot be colored with existing dyes as has happened previously. If new innovation is needed in dye technology and the United States remains a sovereign, free, innovative nation, the U.S. dyes business might again “rise from the ashes” as it has twice previously after two world wars. In the meantime, some of us have fond memories of the “good old days” and are proud and thankful to have been a small part of the U.S. dye industry and the advances in disperse dye chemistry in particular.

References

5. U.S. Patent No. 2,990,413.

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