Chapter 9: The Structure and Properties of Disperse Dyes And Related Topics

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Before leaving the nonionic disperse dyes and their application to man-made fibers for the next topic—the application of ionic dyes to ionic fibers—there are a number of subject areas which merit further examination, and these will be treated in the following order:

- the application of disperse dyes to nylon
- the chemical structure of disperse dyes
- color and constitution of disperse dyes
- gas fading of certain disperse dyes
- commercial products

Application of Disperse Dyes to Nylon

The previous sections have concentrated on the dyeing of disperse dyes onto polyester, for which disperse dyes are used

ABSTRACT

The dyeing of nylon with disperse dyes is briefly reviewed followed by discussion of the chemical structures used for disperse dyes. The importance and versatility of derivatives of aminoazobenzene and anthraquinone is examined and their augmentation by heterocyclic and heterocyclic azo derivatives is illustrated. The relationship between color and constitution of disperse azo and AQ dyes is described in simple terms followed by an account of the fading of disperse dyeings by nitrogen oxides and ozone. The different commercial forms of disperse dye products are introduced and the chemical content of such products is discussed.

KEY TERMS

Aminoazobenzene
Anthraquinone (AQ)
Azo
Color and Constitution
Disperse Dyes
Gas Fading
Heterocyclic Dyes
Nitrogen Oxides
Nylon
Ozone

almost exclusively. The only exception is the use of basic dyes to dye the relatively small percentage of cationic dyeable polyester fibers. This will be treated in a later chapter. Disperse dyes have been and are still being used for a significant segment of the nylon textile business, despite the fact that the most widely used dye application category for nylon dyeing in general is the acid dye category.

Compared with acid dyeings, disperse dyeings on nylon have relatively poor fastness towards wet treatments, as well as ozone and nitrogen oxides. Disperse dyeings on secondary cellulose acetate are even more susceptible to the gas fumes (1). Poor fastness to ozone and nitrogen oxides was discovered quite early (2), with the poor performance of selected anthraquinonoid bright violets and blues on acetate. Further discussion on fastness will be deferred until the chemical structure of disperse dyes has been introduced.

On the credit side, disperse dyes are economical, easy to apply to nylon, and have an outstanding ability to cover morphological and fiber chemistry barré, which makes them particularly valuable for dyeing unbranded nylon; i.e., nylon which includes fibers from different merges or heatsetting lots whose morphology and fiber chemistry is probably not sufficiently close to ensure good barré coverage when fabrics from these fibers are dyed with the preferred acid dyes. Furthermore, disperse dyes do have good buildup to heavy shades. Some of them dye very rapidly, but even these have generally good leveling and migration properties.

The disperse dyes most suitable for nylon cover the range from the low energy early disperse dyes developed for secondary cellulose acetate to those medium energy disperse dyes developed later for application to polyester using either high temperature or carrier. The former group are generally of lower molecular size (relative molecular mass, rmm), dye rapidly, and level particularly well, but have relatively poor wetfastness and tend to sublime from the fiber surfaces. If goods are to be subjected to heat treatment after dyeing—for example, post boarding as practiced in the hosiery trade—dyes with larger molecules and less tendency to

sublime are preferred. However, much of the hosiery trade has moved away from disperse dyes because of their poor wet-fastness on the Lycra polyurethane stretch fibers.

In the carpet trade, about 1-2% of the goods are still dyed with disperse dyes, but the lightfastness and fastness to ozone and nitrogen oxides all need to be very good. Suitable dyes might be C.I. Yellows 3 and 54, Reds 55 and 60 and Blues 56, 60 and 26.

Although disperse dyes are normally applied to nylon between 80-100C (176-212F), some of the higher energy polyester disperse dyes may be applied at temperatures of as much as 110C (240F) on nylon 6 and 120C (258F) on nylon 66.

Chemical Structure of Disperse Dyes

Little of a general nature has changed in disperse dyes during the last 40 years, although much has been progressively modified to provide products with better performance in all phases of the dyeing operation and in the fastness of the dyeings particularly on polyester. Continuous dyeing processes have opened a whole new dimension of dyeing possibilities for polyester/cotton blends.

The largest majority (ca. 50%) of disperse dyes are monoazo dyes of relatively low molecular weights (rmm). They contain no ionic solubilizing groups in dyebath conditions; i.e. they are essentially nonionic, although they may be quite strongly polar. A significant proportion of the remaining disperse dyes are anthraquinonoid (AQ) derivatives, (ca. 25%), but they are being gradually replaced (except for some bright pinks and blues) because of cost and environmental problems in manufacture. Newer disperse dyes are increasingly based on the use of heterocyclic components; i.e., chemical radicals containing five or six membered aromatic rings which include nitrogen, sulfur and oxygen in place of one or more of the normal carbon atoms. These heterocycles may appear at either side of the azo chromophore, although many are chromophores in their own right. For a more detailed treatment, see Ref. (3).

Some of the remaining dyes are unique chemical entities and among the variety of
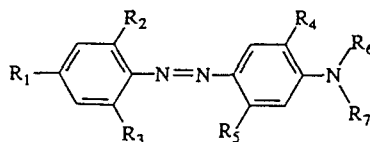
Disperse Dyes

Fig. 1. Structural skeleton of most monoazo disperse dyes.

structural types found suitable for disperse dyes are benzodifuranones, coumarins, methines (styryl or arylidines), naphthalimides, nitrodiphenylamines and quinophthalones. Some of these structures can only be visually identified as disperse dyes by their being free from ionic solubilizing groups, of low rmm, and because they are unmetallized. For the most part disperse dyes have no fiber reactive groups (although there are now some reactive disperse dyes). Certainly for polyester disperse dyes there should be no groups present which will not withstand neutral aqueous hydrolysis at 130C (265F) if they are to be used for high temperature dyeing. It is because of this threat of neutral or more particularly alkaline hydrolysis that many disperse dyes must be dyed inside a fairly narrow range of pH's on the acid side of neutral (4.5-5.0). It has been mentioned previously (4) and elsewhere (5) that suitable dye structures can take advantage of their ease of alkaline hydrolysis. These enable the use of mild clearing procedures after dyeing. One such structure is shown later in Fig. 4a, where hydrolytic cleavage of the dye structure occurs at the dotted line. Another is shown in Fig. 3a.

Monoazo Dyes

Fig. 1 shows the general structure of the majority of monoazo disperse dyes. These are largely based on the parent compound aminoazobenzene, C.I. Solvent Yellow 1, in which all the substituents labeled $R_1 - R_7$ are hydrogen, –H. Aminoazobenzene was found to dye polyester without carrier to an undistinguished shade of yellow with such poor fastness that it is not used as a disperse dye today, even to dye acetate.

The chemical nature of the substituents $R_1 - R_7$ control the characteristics of the disperse dye product, from cost, ease of manufacture through to color, colorfastness and dyeing properties. The parent structure could hypothetically carry four more substituents to replace all the original hydrogens on the aromatic ring carbons, but such substitutions would not be usual.

The extreme versatility of azo dye chemistry and its position as the dominant chromophore in commercial dyes and pigments can easily be illustrated by first listing some of the more conventional groups which could be present at positions $R_1 - R_7$ in the molecule of an aminoazobenzene based disperse dye.

R_1: –H, –NO$_2$, two possibilities;

R_2: –H, –NO$_2$, –CN (cyano), –SO$_2$CH$_3$ (methylsulfonyl), –Br (bromo), –Cl, six possibilities;

R_3: as for R_2;

R_4: –H, –CH$_3$ (methyl), –OCH$_3$ (methoxy), –C$_2$H$_5$ (ethyl), –OC$_2$H$_5$ (ethoxy), five possibilities;

R_5: –H, –CH$_3$, –C$_2$H$_5$, –NHCOCH$_3$ (acetamido), –NHCOC$_2$H$_5$ (propionamido), five possibilities;

R_6: –H, –CH$_3$, –C$_2$H$_5$, –C$_4$H$_9$ (n. butyl), –C$_2$H$_4$OH(hydroxyethyl), –C$_2$H$_4$CN (cyanoethyl), –C$_2$H$_4$OCOCH$_3$ (acetoxyethyl), seven possibilities;

R_7: As for R_6.

Simplistic reasoning says that with the substitution of only this limited number of different chemical radicals (15) into the parent aminoazobenzene structure, 29,400 different structures could be generated—($2 \times 21 \times 5 \times 5 \times 28$, since position $R_2 \equiv R_3$ and $R_6 \equiv R_7$).

In practice, this number is too high

because there are chemical restrictions about which substituents can appear together in the same molecule. On the other hand the number of substituent radicals listed is by no means exhaustive and the addition of others would raise the number of possible combinations.

Whatever the correct number of realistic structural possibilities is, it will be a large number indicating the almost unlimited flexibility of azo chemistry. Furthermore, the range of colors possible will stretch from neutral yellow through orange, brown, red, violet and navy to dull greenish blue. It does not extend to bright blues, greens or blacks. The brighter and greener shades of yellow are well covered by the heterocyclic azo and other possible chromophores, as are the brightest reds and blues. Some examples of aminoazobenzene derivatives are shown in Table I.

There are a few important monoazo dyes based on hydroxyazobenzene, rather than aminoazobenzene; i.e., with no amino group and therefore with no substituents R_6 and R_7; e.g. C.I. Disperse Yellow 3, also shown at the foot of Table I. The hydroxy group imparts better lightfastness to dyeings on acetate and polyester than corresponding amino groups. This same hydroxy group has the reverse effect on nylon dyeings.

Anthraquinonoid (AQ) Dyes

Fig. 2 shows the general structure of the majority of AQ disperse dyes. Substituents $R_1 - R_5$ and R_8 can be varied to produce a number of widely used structures, all of which are noted for their brightness. In principle there are eight carbon atoms with attached hydrogens in the parent anthraquinone molecule. Here the numbering of possible substituents follows the way chemists number the carbon atoms (1–5 and 8) from which the hydrogen is to be displaced. For disperse dyes, placing substituents on the carbon atoms at the six and seven positions has not proved to be valuable. The hue is almost totally controlled by substituents R_1, R_4, R_5 and R_8, and these substituents are usually hydroxy, amino and secondary amino groups, –NHR. The substituent (R) in this secondary amino group can be: –CH$_3$, –C$_2$H$_4$OH, a benzene ring (Ar), or a benzene ring which is itself substituted; e.g., with a methoxy group –OCH$_3$ (ArOMe), or a hydroxyethyl group –C$_2$H$_4$OH (ArEtOH) at the para position (see Table II).

Substituents in the R_2 and R_3 positions have less effect on the hue of the AQ disperse dyes but can have a considerable effect on the dyeing and fastness properties of the product. While yellow and orange products based on anthraquinone can be synthesized, they have not proved to be competitive with yellow and orange disperse dyes based on other chromo-

Table I. Disperse Dye Structures Based on Aminoazobenzene

Dye #	C.I. Disperse Dye Name	R_1[a]	R_2	R_3	R_4	R_5	R_6	R_7
1	Yellow[b]	H	H	H	H	H	H	H
2	Orange 3	NO$_2$	H	H	H	H	H	H
3	Orange 30	NO$_2$	Cl	Cl	H	H	C$_2$H$_4$CN	C$_2$H$_4$OAc[c]
4	Red 1	NO$_2$	H	H	H	H	C$_2$H$_5$	C$_2$H$_4$OH
5	Red 13	NO$_2$	Cl	H	H	H	C$_2$H$_5$	C$_2$H$_4$OH
6	Red 195	NO$_2$	SO$_2$CH$_3$	H	H	CH$_3$	C$_2$H$_4$OAc	C$_2$H$_4$OAc
7	Violet 12	NO$_2$	NO$_2$	H	H	H	C$_4$H$_9$	C$_2$H$_4$OH
8	Violet 33	NO$_2$	CN	H	H	CH$_3$	C$_2$H$_4$OAc	C$_2$H$_4$OAc
9	Blue 79	NO$_2$	NO$_2$	Br	OC$_2$H$_5$	NHAc	C$_2$H$_4$OAc	C$_2$H$_4$OAc
10	Yellow 3	AcNH	H	H	CH$_3$	OH	—[d]	—

[a]See Fig. 1 for position of R groups. [b]C.I. Solvent Yellow 1. [c]Ac=acetyl (—COCH$_3$). [d]No—N(R$_6$)R$_7$ group: just H.
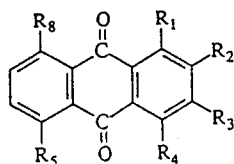
Fig. 2. Structural skeleton of most anthraquinonoid (AQ) disperse dyes.

phores. As a result, most surviving AQ disperse dyes are bright reds, through violets to blues (see Table II). These have only about one half as much color inherent in each molecule as dyes synthesized around azo chromophores. Such color characteristics can be measured in terms of the molar extinction coefficient, ϵ, which is also known as the molar absorptivity coefficient, a. A number of anthraquinonoid disperse dye structures are shown in Table II.

Other Dye Chromophores

The color ranges of disperse dyes based on aminoazobenzene and anthraquinone are very broad, but are not without limitations. The aminoazobenzene derivatives do not extend into the area of greenish yellows. Although they are often economical and show high extinction coefficients (ϵ), they are not noted for their brightness. Similarly, derivatives of anthraquinone suitable for bright greenish yellows can be synthesized, but there are other more cost effective alternatives because AQ dyes generally have much lower extinction coefficients than azo dyes. To date there have been no general purpose true green disperse dyes. Chemists have sought to counter these deficiencies in brightness, color range, and economics with a large number of different chemical types of disperse dyes, and some of these are illustrated in Figs. 3 and 4. Fig. 3 shows the following chemical structures as examples:

● Benzodifuranes: Derivatives of a recently introduced heterocyclic chromophore boast a bright red disperse dye, C.I. Disperse Red 356 (6), of very high extinction coefficient. Hues range from yellow to blue (7).

● Coumarins: Principally bright fluorescent yellows; e.g. C.I. Disperse Yellow 82. Some derivatives are used as fluorescent brighteners.

● Methines: Although mainly featured in brilliant yellows; e.g. C.I. Disperse Yellows 49, 82, 92, the group includes the brightest blue disperse dye currently available—C.I. Disperse Blue 354.

● Naphthalimides: This group includes some brilliant, fluorescent compounds, an early example being C.I. Disperse Yellow 11.
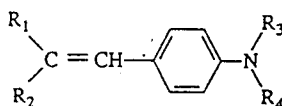
● Nitrodiphenylamines: These yellow dyes are chemically simple, economical yellows of high lightfastness on polyester, but of low extinction coefficients. They
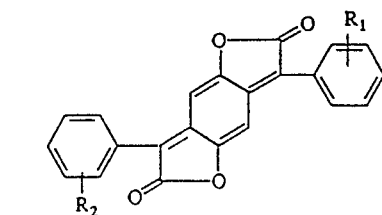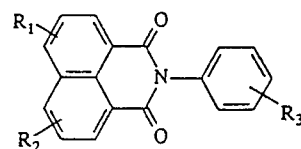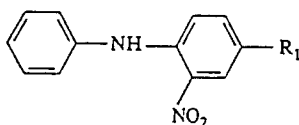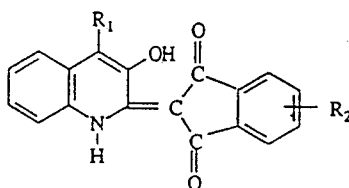

a) benzodifuranes
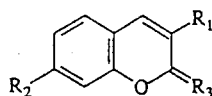
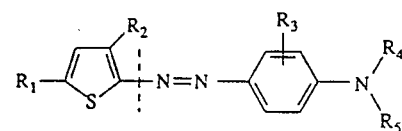b) coumarins

c) methines

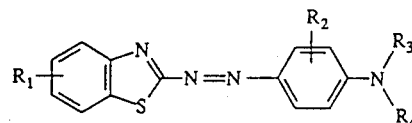d) naphthalimides

e) nitrodiphenylamines

f) quinophthalones

Fig. 3. Miscellaneous structures used in disperse dyes.
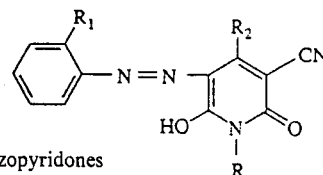
have poor lightfastness on nylon. Examples are C.I. Disperse Yellows 33, 42, 59 and 86.

a) azothiophenes

b) azobenzothiazoles

c) azopyridones

Fig. 4. Monoazo disperse dyes with heterocyclic structures.

● Quinophthalones: The unsubstituted parent compound, C.I. Disperse Yellow 54, is a low energy dye suitable for many general applications, often along with C.I. Disperse Red 60 and C.I. Disperse Blue 56. Substituted derivatives C.I. Disperse Yellows 64 and 67 have higher energy and have better resistance to sublimation.

Fig. 4 illustrates three general examples of heterocyclic diazo components (4 a, b) and coupling components (4c) which have been used to improve the brightness and color range of monoazo disperse dyes. Many other heterocycles have been used, but here are shown only:

● Azothiophenes: These range from C.I. Disperse Blue 284 to the only available disperse green, C.I. Disperse Green 9.

● Azobenzothiazoles: Noteworthy for scarlets through bordeaux reds which include C.I. Disperse Reds 153, 177, 263.

● Azopyridones: Often used for bright yellows; e.g., C.I. Yellow 119.

Color and Constitution in Azo and AQ Disperse Dyes

Study of the relationship between the color

Table II. Disperse Dye Structures Based on Anthraquinone

Dye #	C.I. Disperse Dye Name	R1[a]	R2	R3	R4	R5	R8
1	Orange[b]	OH	H	H	OH	H	H
2	Red 15	NH2	H	H	OH	H	H
3	Red 9	NHCH3	H	H	H	H	H
4	Red 60	NH2	OAr	H	OH	H	H
5	Violet 1	NH2	H	H	NH2	H	H
6	Blue 1	NH2	H	H	NH2	NH2	NH2
7	Blue 14	NHCH3	H	H	NHCH3	H	H
8	Blue 3	NHCH3	H	H	NHC2H4OH	H	H
9	Blue 24	NHCH3	H	H	NHAr	H	H
10	Blue 27	OH	H	H	NHArEtOH	NO2	OH
11	Blue 56	OH	Brn[c]	H	NH2	OH	NH2
12	Blue 73	OH	ArOMe	H	NH2	OH	NH2
13	Blue 60	NH2	CO—N(R)—CO[d]		NH2	H	H

[a]See Fig. 2 for positions of R groups. [b]The orange intermediate Quinizarin. [c]Brn. The positions and number of bromo groups is uncertain. [d]This group bridges the R2-R3 positions and R is C3H6OCH3.

Disperse Dyes

and constitution of molecules can involve complex concepts which are inappropriate for discussion here; e.g., see Ref. (8). The treatment here will be simple and limited to azobenzene and anthraquinone chromophores. Even so, it is first necessary to introduce a concept, which will be new to non-chemists. This is the idea that different chemical substituent groups in dye molecules change the color of the dyes because of their tendency to either accept electrons or donate electrons. The two chromophores are treated separately.

Azo Disperse Dyes

In disperse monoazo dyes, the part of the molecule which was originally the diazo component (9), is conventionally drawn at the left hand side of the azo group. This side of the molecule normally contains the groups tending to attract electrons, R_1-R_3. The part of the molecule which was the coupling component (9), conventionally drawn at the right hand side, contains groups which tend to donate electrons, such as the substituted amino groups, $-N(R_6)R_7$.

The greater the tendency of groups at the left side of the azo group to accept electrons and the groups at the right hand side to donate electrons, the further the hue of the molecule will lie along the line from yellow, orange, red, violet, blue to green and even black. Movement along the line in the direction yellow to black is called a bathochromic shift. In more precise terms, a bathochromic shift is an increase in the wavelength of maximum (light) absorption by the dye. Shade cards are normally presented in bathochromic order, the color of each successive dyeing being shifted bathochromically relative to its predecessor. Movement in the opposite direction, black to yellow, is called a hypsochromic shift; i.e., the wavelength of maximum absorption is decreased.

Arranged in approximate order of the decreasing effect are the groups which attract electrons strongly; e.g., $-NO_2$ (nitro) > $-CN$ (cyano) > $-SO_2CH_3$ (methyl sulfonyl) groups, followed by the $-Br$ (bromo) and $-Cl$ (chloro) groups. Groups which donate electrons most strongly are the alkyl substituted amines; e.g., $-N(CH_3)_2$ (dimethylamino) > $-NHCH_3$ (methylamino) > $-NH_2$ (amino) groups followed by the $-OH$ (hydroxy) group. The less strongly electron donating groups are $-CH_3$ (methyl), $-C_2H_5$ (ethyl), $-OCH_3$ (methoxy), and $-OC_2H_5$ (ethoxy), while $-H$ and $-NHCOCH_3$ (acetylamino) are neither donors nor acceptors.

Examining Table I, the dyes (except for #11, C.I. Direct Yellow 3) are listed as a more or less bathochromic series following the order they might appear in a dye manufacturer's shade card. As the combined effects of substituents $R_1 - R_3$ increase in electron accepting capacity, the hue of the dyes moves from yellow to blue, from dye #1-dye #9.

To see the effect of alkyl substitution in the amino group (R_6, R_7) compare dyes #2 and #4. The addition of the C_2H_5 (ethyl) and C_2H_4OH (hydroxyethyl) substituents are the difference between C.I. Disperse Orange 3 and C.I. Disperse Red 1. However, among those dyes #3-9, the differences between the effects of the different alkyl substituents is not particularly marked.

AQ Disperse Dyes

In the anthraquinone series the source of the hue is similar to that in the azo series. This time it is the interaction between the electron accepting groups of the chromophore itself; i.e., the two anthraquinone carbonyl groups, $>C = O$, and electron donating substituent groups in the 1, 4, 5 and 8 positions (R_1, R_4, R_5, R_8).

The electron donating groups are usually primary amines ($-NH_2$), secondary amines ($-NHR$) where R can be an arylamino derivative and hydroxy groups. (Tertiary amines do not lead to satisfactory dye structures for they are bulky and eliminate the possibility of hydrogen bonding between adjacent amino and carbonyl groups $>N-H...O = C<$). The extent to which electron donor groups affect the hue lies in the order given previously, except that (unexpectedly) the arylamino group heads the list: $-NHAr>-NHAlk>-NH_2>-OH$. The more powerful the effect of the electron donor substituents, the more marked is the bathochromic shift (in the direction yellow to black), while substitution in both the benzenoid rings of anthraquinone, R_1, R_4, R_5, and R_8 is more effective than substitution in only one. The appropriate substituents at the R_2 and R_3 positions can be used to augment desired properties of the dye molecule; e.g., lightfastness.

The effects of some of the different substituents are shown in Table II, which are listed in a more or less bathochromic order from top to bottom. Here progressive substitutions of the R_1, R_4, R_5 and R_8 positions with $-OH$ and $-NH_2$ groups carry the color from the orange intermediate (Quinizarin), dye #1 through the red dye #2 (C.I. Disperse Red 15), violet dye #6 (C.I. Disperse Violet 1), to the blue dye #7 (C.I. Disperse Blue 1) with four donor groups.

The powerful effect of the methylamino groups at R_1 can be seen by comparing the color of dye #2 with both $-OH$ and $-NH_2$ substituents with dye #3, which has only the $-NHCH_3$ substituent. Also, dyes #7

and #8 require only two secondary amino substituents to be blue, cf. dye #6 with four amino groups.

Gas Fading of Certain Disperse Dyes

The fading of certain anthraquinonoid disperse violet and blue dyes, by low concentrations of nitrogen oxides produced during combustion of various fuels, is most severe with dyeings on secondary cellulose acetate (acetate). The importance of this problem was appreciated before 1950 (2).

Such fading is intrinsically less severe on nylon; but the present expectation of very high levels of colorfastness on home furnishings and carpeting, particularly automotive carpeting, coupled with the wideness of their distribution has made it imperative to be able to dye nylon to shades of very high resistance to fading by nitrogen oxides and ozone. Current U.S. test methods (1) involve two different conditions of humidity and temperature: 87.5% RH, 40C (104F); and 67% RH, 18-28C (64-82F).

Salvin and coworkers (2) showed that the resistance of dyeings on acetate to gas fume fading by nitrogen oxides was related to the resistance of the $-NHR$ groups (in some of the AQ disperse dyes) towards chemical attack by the fumes. This is, in turn, related to the basicity of the $-NHR$ group on the dyes.

Standard dyeings on acetate, at 0.4% owg of a specific one of the generic prototypes of C.I. Disperse Blue 3, are used as fading test controls. The need to define a particular product is because of the nature of the manufacturing process for C.I. Disperse Blue 3. Despite the idealized structure shown at dye #8 in Table II, commercial products are normally mixtures of dyes in which the $-NHR$ groups can be either $-NHCH_3$ (methylamino) or $-NHC_2H_4OH$ (hydroxyethylamino). One of the possible dyes in the mixture is dye #7 in Table II, C.I. Disperse Blue 14; another is C.I. Disperse Blue 23, where both substituted amines are hydroxyethylamines $-NHC_2H_4OH$. Incidentally, this hydroxyethylamino group is responsible for improving the sublimation fastness of C.I. Disperse Blue 23 dyeings over those of C.I. Disperse Blue 14.

Substitution of the arylamino group $-NHAr$, when Ar is a substituted or unsubstituted phenyl (benzene) ring, for one of the methylamino groups in C.I. Disperse Blue 14, gives dye #9, Table II, C.I. Disperse Blue 24. This dye is less susceptible than C.I. Disperse Blue 14 to attack by nitrogen oxides but has poorer dyeing properties.

A better solution to the problem would be to select a much more gas fume resistant dye such as dye #10, C.I. Disperse Blue 27, with better dyeing properties than the C.I. Disperse Blue 24.

Gas fume fading of the blue alkylamino AQ disperse dyes by nitrogen oxides results in a reddening of the shade, due first to nitrosation and then replacement of the alkylamino group by a hydroxy group (10).

Ozone is a more powerful oxidizing agent than nitrogen oxides and is not satisfied with destroying the substituent but destroys the anthraquinone structure as well (11). A forthcoming publication (12) will deal specifically with overcoming the ozone fading of nylon carpets.

Colorless chemicals known as fading inhibitors, with some substantivity for acetate fibers, have been developed. These are simple organic materials of high basicity which work by preferentially reacting with nitrogen oxides thereby offering a degree of protection to the dyes. In the case of nylon fabrics in which gas fading is a problem, the more conventional solution is to switch to acid dyes, which are less susceptible to fade. More recently selected AQ fiber reactive blues have been evaluated and are quite resistant even to fading by ozone.

Commercial Products

Disperse dyes are sold in three principle forms—powders, grains and pastes. Solid forms (powders and grains) constitute about two thirds of the total dye sold. Each form has its inherent advantages.

Powders are the most prone to dusting in the drug room but the dusting cannot be considered severe when compared with the dusting properties of many of the much more water soluble ionic dyes. Dusting can be controlled by incorporation of small amounts of oil, such as Bay or Twitchell, into the powder.

Grains are more free from dust than powders. Their pouring characteristics and ease of weighing makes them a valuable adjunct to the more common powder form.

Pastes, sometimes called liquids, constitute approximately one third of the disperse dyes sold. These go mainly to continuous dyehouses where any poorly dispersed particles in the feed tanks would inevitably result in specks and spots in the dyed goods. With stored pastes, it is important to prevent sedimentation, and arrangements are usually made for gentle stirring in those dye drums which have been opened.

Most powders and grains contain about 30% by weight of the active dye material, the rest being made up of processing aids, inert diluents, dispersing agents, antidusting oils and shading colors where necessary. By contrast, pastes have traditionally contained only half as much active dye or about 15% of the total weight. If any product is offered at an unusual strength, it should be indicated as a part of the product name. Unless otherwise mentioned, the product is assumed to be a 100% powder. A designation 150% means a powder 50% stronger than the seller's standard powder and contains more active dye. Pastes are normally assumed to be only ca. 50% of the strength of the standard powder so 100% paste (or liquid) means paste equal to the strength of the standard powder but twice the strength of the normal paste.

Dye Mixtures

Black disperse dyes are usually mixtures of three components—a navy, a red or rubine and a yellow-brown or dull orange. Many disperse dyes are mixtures which result from the nature of their manufacturing processes; e.g., C.I. Disperse Red 153, C.I. Disperse Blues 3 and 281. Some dyes contain shading colors added during standardization.

Thin layer chromatography (TLC) is a good way to rapidly examine the makeup of disperse dyes. Dyes dissolved in methylene chloride or acetone can be spotted onto silica gel sheets (e.g., Kodak Chromagram Sheets), the solvent evaporated and the dry dye spot eluted with a 90:10 benzene: acetone mixture (13). Care should be taken when interpreting the resulting chromatogram. Multiple spots may originate from the same commercial dye—some of the spots may be impurities and byproducts, some may be an indication of the method of manufacture and still others may be shading colors used in standardization.

The same TLC technique is also useful for investigating the individual colors which went into a disperse dyeing. Methylene chloride is a good solvent for extracting disperse dyes from polyester while 50/50 DMF/water (dimethyl formamide) and MEK (methyl ethyl ketone) are suitable solvents to extract disperse dyes from nylon.

The Dispersion

Disperse dyes must be ground to an extremely fine particle size distribution in order for them to be applied without specks or spots, and in order that they may dissolve into the dyebath without hampering the rate of uptake of the dye. A qualitative test method using filter papers is available for determining whether the particle size distribution of a product is in a satisfactory range (14). However, such tests should not be regarded as a reliable predictor of whether a dye will perform well in a particular dyeing process. If the results are very poor, it is probable that dyeing performance will also be poor. When checking the dispersion characteristics of different batches of the same product, what is important is that the results are consistent from batch to batch.

When disperse dyes are used for package or jet dyeing at high temperatures, the shearing forces and thermal stresses on the dispersion can be severe. It would be highly desirable to be able to predict whether particular dispersions were able to withstand particular dyeing conditions, or whether they would breakdown, and by so doing cause problems in the dyed goods. Unfortunately, the state of the dispersion in dyeing systems is not static and is complicated by the presence of the goods. Another complicating factor is the excellent dyeing properties of some dyes; e.g., C.I. Disperse Red 60, whose dispersions can break down quite readily. Particulate migration (15), the tendency of dispersions padded on goods to migrate on drying, will also be affected by variations in the particle size distribution of the dispersion.

Review

The dyeing of nylon with disperse dyes, a gradually shrinking segment of the dyeing business, has been briefly discussed. This was followed by an examination of the chemical structures used as the primary building blocks for the disperse dyes. The effects of changing the substituents in the aminoazobenzene and anthraquinone based disperse dyes was discussed as an example of the relationship between dye color and constitution. The fading of violet and blue AQ dyes on exposure to nitrogen oxides and ozone was discussed in reference to the dye structure. The nature of commercial disperse dye products was introduced and the importance of the dispersion and dispersion stability touched upon. The foregoing sections round out the treatment of the application of nonionic dyes to man-made fibers.   ∞

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