Chapter 12: The Application of Basic Dye Cations to Anionic Fibers: Dyeing Acrylic and Other Fibers with Basic Dyes

By J. R. ASPLAND, School of Textiles, Clemson University, Clemson, S. C.

The dyeing of wool, silk and nylon fibers was discussed in chapter 11. The ionic characteristics of these fibers in dyebath conditions are strongly dependent on pH. As the bath pH falls below neutral, becoming increasingly acidic, the overall charge on the fiber molecules becomes more and more positive or cationic. Consequently anionic dyes with opposite charge have increasing substantivity for these fibers as the dyebath pH falls.

In this chapter our principle concern is with acrylic and modacrylic fibers which contain groups which dissociate in dyebaths to produce negatively charged fiber anions. These fibers are attracted to cations, colored or colorless—e.g., basic dyes or cationic levelers—which can be introduced into the dyebath. Secondary concerns are the dyeing of cationic-dyeable polyester and cationic-dyeable nylon variants. There are only a few naturally occurring fibrous materials for which methods of dyeing with basic dyes have not

ABSTRACT

The development of basic-dyeable acrylic fibers and the subsequent rejuvenation of the basic dye application category are discussed. On acrylic fibers, basic dyes can dye very rapidly above the glass transition temperature with the consequent risk of unlevelness. Means to overcome the problem are outlined. The variety of cationic dye chromophores is introduced.

KEY TERMS

Acrylic Fibers
Basic Dyes
Combination Constant
Dye Rate Compatibility
Dye Saturation Factor
Dyeing
Fiber Saturation Value
Levelers
Retarders

been developed. Use of basic dyeing methods has been restricted by the poor fastness properties of the resultant dyeings. In the U.S. today the use of basic dyes on such natural fiber substrates is largely restricted to some leather and paper dyeing. There is still a little basic dyeing of silk and secondary cellulose acetate fabrics for such applications as linings where the wetfastness and lightfastness of dyeings may not be critical.

There are good reasons why members of this basic dye application category were once used for so many purposes and why their present day uses are relatively restricted.

Basic Dyes:
Historical and General

Mauveine, the first synthetic dye, was discovered in 1856 and was a basic dye. In common with many of its successors, it was notable for its brilliance of shade, high tinctorial strength, water solubility and poor fastness properties. It was this sheer brilliance which helped to spur the growth of the embryonic synthetic dye industry and within a generation most of the dull (drab) natural dyes known for millennia had been swept aside by the new synthetic or aniline dyes.

New methods had to be devised for application of these basic dyes to the available natural fibers. For cotton they involved the application of tannin (tannic acid) which could be fixed using a suitable metal salt (tartar emetic) followed by application of the dye. In this method the tannic acid complex on the fiber serves as a mordant with which the basic dyes can interact.

To get a qualitative idea of how this mordant dyeing process works, it is only necessary to appreciate that basic dyes are salts (like acid dyes) and dissociate in water to give anions and cations. In basic dyes (unlike acid dyes) the colored part of the salt is the cation (+) which is why they are frequently referred to as cationic dyes. The associated anion (−) can be something as simple as a chloride ion. Thus solid basic dyes can be represented by a general formula: $Dye^{\oplus}X^{\ominus}$, where $X^{\ominus}$ can be any of

a number of relatively simple colorless anions.

In water the salt dissociates into colored $Dye^{\oplus}$ cations and the equivalent number of anions. It is very rare for these colored basic dye cations to have more than one positive charge. This contrasts with acid dye anions which can have as many as four or more negative charges.

Cotton fibers treated with tannins have included tannic acid anions which are attractive to basic dye cations. The cotton is said to have been mordanted. Treatment of the mordanted cotton with basic dyes results in the formation of water insoluble ionic complexes on the fiber by interaction of the tannic acid anions and the basic dye cations. Contrast this with the use of backtanning to improve the wetfastness of acid dyeings on nylon (1) where the anionic character of the tannin derivatives at the fiber surface repels any colored dye anions attempting to migrate out of the fiber.

Large amounts of the soluble basic dyes are used in the manufacture of pigments. The pigments are cation/anion salt complexes similar to the color present on mordanted cotton dyed with basic dyes. In this case the basic dye cation replaces the hydrogen ion in complicated inorganic phospho-tungsto-molybdic acids to give water insoluble, pigmentary complex salts with very large molecules.

Despite their wonderful colors, the poor lightfastness of many of the early synthetic or aniline dyes gave a bad name to synthetic dyes in general. The poor performers were notably the basic dyes and the acid dyes for wool derived from the same chromophores. This ill repute has proved hard to outlive despite the fact that there are many synthetic dye products which give dyeings of fastness properties impossible to achieve with natural dyes. If you don't believe it, all you have to do is visit an oriental rug merchant. The first thing he will tell you about a carpet or rug is that it is dyed with natural dyes not aniline dyes. This backhanded slur on synthetic dyes can no longer be justified but has become a part of oriental carpet lore. With experience, a glance at the

Basic Dyes

brightness and uniformity of orange or green areas in such carpets might give contrary indications because there are no true natural green or bright orange dyes.

Through the early decades of the 20th century the end-use performance of synthetic dyes gradually improved, notably with the introduction of more and more anthraquinonoid (nonindigoid) vat dyes. But the retrieval of the poor reputation of the brilliant dyes and their chromophores had to wait another 50 years, until after the introduction of suitably modified polyacrylonitrile fibers.

Acrylic Fibers:
Historical and General

Several polymers had been derived from the acrylonitrile monomers, $CH_2 = CH - CN$, as early as 1930. The reaction is called addition polymerization and involves the vinyl (or substituted vinyl) groups, $CH_2 = C<$, present in the monomers. These add onto one another with opening of the carbon-carbon double bonds, forming long molecular chains as represented in Fig. 1. There is no elimination of small molecules, as in condensation polymerization, which is typified by the reactions to form polyester and polyamides. For the early polyacrylonitriles, the substituents in Fig. 1, R_1 and R_2, were restricted to hydrogen, $-H$, and the cyano (or nitrilo) group, $-CN$, respectively.

However there were serious technical problems to be solved before these polymers could be spun into fibers. Solvent spinning was hampered by the difficulty of finding suitable solvents. Melt spinning was a problem because the polymers began to decompose within a few degrees of their melting point.

Then it was discovered that the highly polar water soluble solvents such as dimethyl formamide (DMF) and concentrated aqueous solutions of some salts would dissolve the polyacrylonitriles. The discovery led to the introduction of the first commercial acrylic fibers in 1949. In common with polyester fibers, they proved hard to dye. In retrospect this does not seem surprising since they were both hydrophobic and had a glass transition temperature (T_g) above the atmospheric boil. The moisture regain at 65% RH and 20C (68F) was 1 to 2% and T_g was 104C (220F).

In due course it was found that when nonionic comonomers such as methyl methacrylate, methyl acrylate and vinyl acetate were added, the T_g could be lowered to ca. 75-85C (165-185F). The structure of various comonomers are given in Table I. The consequent structural disruption and loosening of the fiber-fiber bonds made for easier dye diffusion and also made the polymer easier to dissolve in suitable solvents.

Table I. Some Substituents in Acrylic and Modacrylic Fiber Comonomers

Comonomer Name and Nature	$CH_2 = C(R_1) - R_2$ Substituents	
	R_1	R_2
Neutral		
Methyl Acrylate	$-H$	$-CO-O-CH_3$
Methyl Methacrylate	$-CH_3$	$-CO-O-CH_3$
Vinyl Acetate	$-H$	$-O-CO-CH_3$
Anionic		
Allyl Sulfonate	$-H$	$-CH_2-SO_3^\ominus$
Methallyl Sulfonate	$-CH_3$	$-CH_2-SO_3^\ominus$
Styrene Sulfonate	$-H$	$-C_6H_5-SO_3^\ominus$
Itaconic Acid	$-COOH$	$-CH_2-COOH$
Neutral (FR Properties)		
Vinyl Chloride/ Bromide	$-H$	$-Cl/Br$
Vinylidene Chloride	$-Cl$	$-Cl$

The further addition of comonomers from aliphatic and aromatic (benzenoid) vinyl sulfonates, such as methallyl and styrene sulfonates (Table I), ensured that the fibers would be permanently anionic and bear negative charges; i.e., $-SO_3^\ominus$ except at extremely low pH's. The negative charges underwrite the electrostatic (or coulombic) attraction of the fibers for the colored basic dye cations and for colorless cations as well.

Other potentially anionic comonomers include carboxylic acids with substituted vinyl groups, such as itaconic acid. But like all weak acids, the extent to which they dissociate into anions (in this case, carboxylate ions, $-CO_2^\ominus$ is dependent on their
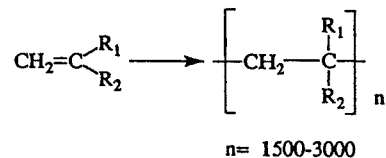
Fig. 1. Addition polymerization of acrylonitrile and related comonomers.

$$n= 1500-3000$$

acidic dissociation constants, K_a. This is completely analogous to the situation with the carboxylic acid groups in nylon, silk and wool (2). Normally, as the pH falls below the pK_a, the carboxylate group concentration falls rapidly for two pH units; above the pK_a, the carboxylate group concentration rises rapidly for two pH units. (The situation is more complex with dibasic acids, such as itaconic acid, which has two pK_a values.) Incidentally, cation-forming comonomers with their intrinsic attraction for acid dye anions have also been used, but have met with limited commercial success.

Sodium bisulfite and potassium persulfate, present as polymerization (redox) catalysts, are responsible for the generation of additional sulfate, $-OSO_3^\ominus$, and sulfonate anions, which can be found at the end of the polymer chains.

Despite the miscellany of possible comonomers and the adventitious end groups, by far the largest portion of the regular acrylic fiber is made up of polyacrylonitrile. Acrylic fibers are defined by the U.S. Federal Trade Commission as those fibers produced from 85% or more acrylonitrile monomer.

Modacrylic fibers are acrylic fibers which have included more than 15% but less than 65% of alternative comonomers to achieve particular properties such as improved flame retardancy. The additional comonomers are normally vinyl chloride or vinylidene chloride, Table I, and for the optimal effect they should be present as 30 to 60% of total monomer. In fact, they could be present at higher concentrations than the acrylonitrile. However, since modacrylic fibers constitute less than 20% of the total acrylic fiber market and since their dyeing properties are substantially the same as those of acrylic fibers, no effort will be made to differentiate between them in subsequent discussion of dyeing.

Acrylic fibers are generally produced by extrusion of solutions of the polymers, followed by removal of the solvent. The latter can be accomplished either by evaporation (dry spinning) or by washing out the solvent (wet spinning). Produced either way, the fibers are then drawn and heat set. Dry spun fibers are often recognizable by dog bone shaped cross sections where wet spun fibers are usually oval or near circular.

The morphology, particularly the microscopic structure of wet spun filaments, can be very different from that of dry spun
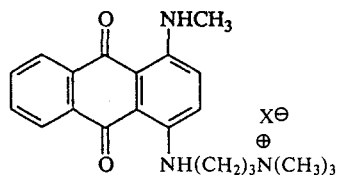
Fig. 2. AQ; e.g., C.I. Basic Blue 22.

Fig. 3. Azo; e.g., C.I. Basic Red 18 type.

fibers. Wet spun fibers contain large numbers of small voids, which make the fibers more accessible to the chemicals in the dyebath. These voids can also adversely affect the apparent depth of color per unit of dye on the fiber, all other fiber variables being equal, a rare occurrence.

A result of all the possible differences in monomers, monomer ionic character, proportions of monomer in the polymer, polymerization conditions, spinning methods and heatsetting conditions, is the large number of different acrylic and modacrylic fibers in the marketplace.

The practical dyer should be aware of the wide range of dyeing properties possible between different types of acrylic fibers. Taking a systematic approach to dyeing acrylic the dyer can take the variations in stride. A definitive text covers this subject (3).

Properties and End Uses

Acrylic fibers are resistant to attack by most common chemicals (with the exception of a few solvents, such as hot DMF) and are considered inert. They are hydrophobic, resist degradation by light, soften above their glass transition temperature and can be dyed to an extraordinarily wide range of shades of very good fastness properties with the historically maligned basic dyes. The good lightfastness can be attributed to the hydrophobicity of the fibers, for it has been shown that the absence of water molecules materially reduces the rate of light fading. Acrylic can also be dyed with disperse dyes but only in light to medium shades of moderate fastness.

Due to their desirable features, acrylics and modacrylics find a wide variety of end uses in apparel and home furnishings. One such feature is acrylic's warm soft hand, which has been compared to that of wool although there is no real substitute for wool. Acrylics are intrinsically resistant to light, insect larvae and microbiological attack, and modacrylics have flame retardant properties which make them suitable for children's sleepwear, upholstery and drapes.

The apparel sector, comprised of about 200 million pounds in 1990, is directed towards such items as hose, socks, sweaters, accessories, robes and loungewear. Also included in this sector are a variety of top and bottomweight fabrics, craft yarns and high pile fabrics. The apparel sector is comprised of ca. 85% knitgoods, 13% craft yarns and less than 1% woven goods.
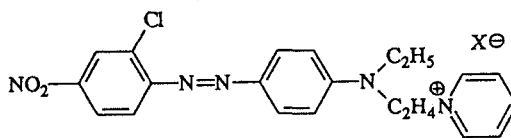
The home furnishings sector, comprising some 63 million pounds per year, includes blankets, draperies, upholstery and slipcovers, as well as carpets and rugs. Carpets and rugs, followed closely by nonwoven blankets, between them comprise 95% of this segment.

U.S. consumption of domestically produced acrylic and modacrylic, staple and tow totaled ca. 350 million pounds in 1990 while 150 million pounds were exported. This gave the acrylic fibers a significant but modest 2% to 3% share of the U.S. mill consumption of fibers divided between a variety of fiber variants. This makes acrylic fibers the third largest group of synthetic fibers in the U.S., but they fall way behind the front runners, polyester and nylon, which each hold a 30% market share.

General Dyeing Mechanism

The general dyeing mechanism for acrylic is identical to all the previous dye application categories examined. The dyeing takes place by the successive steps of sorption at the fiber surfaces, diffusion into the fiber and fixation or retention of the dye by the fiber. However, in the case of dyeing acrylic fiber with cationic dyes, several factors combine to make the overall process slightly different—dye sorption, diffusion from the surface and dye fixation.

● Dye Sorption: Sorption of basic dye cations at fiber surfaces can be expected to occur at a particularly rapid pace. This is due to the surface negative potential associated with the immersion of all fibers in water and sometimes referred to as the zeta potential. Consequently the intrinsic coulombic attraction of the dye cations for the anions of the fiber substrate is enhanced. Saturation of the immediate fiber surface takes place very rapidly unless there is insufficient dye in the bath.

● Diffusion from the Surface: Below the glass transition temperature (T_g)—i.e., below 70-80C (160-175F)—dye diffusion in the fiber is slow due largely to the lack of mobility in the polymer segments but also due to the strong attraction between the fiber anions and the dye cations.

With the exception of dyeings using very small percentages of dye, the diffusion stage takes place when a layer of color saturates the fiber surfaces and maintains a constant dye concentration. Therefore the early rate of dyeing is practically independent of the concentration of dye remaining in the dyebath. This means the rate is independent of the liquor ratio.

Once above the glass transition temperature, the rate of dyeing increases extremely rapidly. The rate of dyeing acrylic doubles every 2.5-3C (4.5-5.5F); whereas for polyester and nylon, when dyed with disperse and acid dyes, the corresponding temperature increases are about 5C (9F) and 10C (18F), respectively (3). Extreme care should be taken in the temperature range just above the glass transition temperature to ensure that the rapidly accelerating rate of dyeing does not lead to unlevelness. This is particularly important since the majority of basic dyes level quite poorly although there are some newer dyes with less substantivity and generally smaller molecules (lower rmm) which level much better. If unlevelness does occur, thermoplasticity of the fibers makes it dangerous to attempt leveling at high temperature or by extending the normal dyeing time.

The high wetfastness of basic dyes on acrylic fibers can be attributed to the fact that most washing procedures take place well below the glass transition temperature when the dye is for all practical purposes trapped inside the hydrophobic fiber.

In practical dyeing during both the surface sorption and dye diffusion phases, it is important that the dyes used are compatible; i.e., that they exhaust at the same or very similar rates, and that the rates are not too high to preclude level dyeing. Both of these aspects of basic dyeing will be discussed.

● Dye Fixation: It is easy to think of basic (cationic) dyeing of acrylic fibers with their anionic charges taking place by means of a glorified ion exchange mechanism. It may be more convenient to think of it this way rather than as another complex (Donnan) ion distribution problem like that for nylon (4,5). Certainly the sorption and diffusion processes are significantly different from those of acid dyes on nylon and overdyeing seems to be less prevalent.

The concentrations of anionic groups in acrylic fibers are generally quite low and are largely made up of permanently anionic groups, $-SO_3^{\ominus}$ and $-OSO_3^{\ominus}$, with no equivalent fiber cationic groups. These anionic groups do not change in concentration with changing pH in the dyebath range. Only those fibers containing carboxylic acid groups have concentrations of anions which are pH dependent, increasing with increasing pH. For example, dibasic itaconic acid with its two carboxy groups, as listed in Table I, is only completely ionized above pH 7.45. Below pH
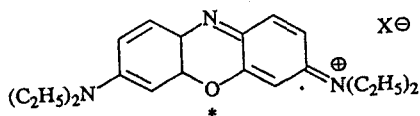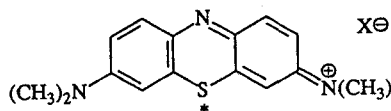
Fig. 4. Oxazines; e.g., C.I. Basic Blue 3.

Fig. 5. Thiazines; e.g., C.I. Basic Blue 9.

Fig. 6. Xanthenes; e.g., C.I. Basic Violet 10.

Fig. 7. Triphenylmethanes, TPM; e.g., C.I. Basic Green 4.

1.85 it is essentially only in the free acid form, ($pK_{a1} = 3.85$, $pK_{a2} = 5.45$).

The practical problem regarding the fixation stage of dyeing is how to avoid trying to put more dye on the fibers than the total concentration of anions in the fiber will permit. This will also be discussed.

Dyeing: General Background

The background to acrylic dyeing can be found described in many places in the literature and in dye manufacturers' publications. The coverage ranges from extensive, authoritative and complete (3) to short, sweet and to the point (6).

A dyeing procedure is the result of an appropriate combination of chemicals (the recipe or formulation) and the dyeing cycle in which they are brought into conjunction with the fiber. The dyebath chemicals and the dyeing cycle will be examined separately. But first, a reminder of the importance of the predyeing wet processes—preparation and bleaching.

Preparation:
Scouring and Bleaching

Poor preparation is the single largest cause of second quality dyeings. Preparation is not always essential, but always desirable. Economics always dictate processing choices, but the possibility of off quality goods should be part of the economic evaluation.

Acrylics can be freed from most lubricants and other fiber processing aids by a single scour with alkali in the form of either ammonia or tetrasodium pyrophosphate, TSPP, both 0.5-1.0% owg, together with a nonionic surfactant (ca. 1.0% owg). Treatment for 15-30 minutes at 140-160F (60-70C) followed by warm and cold rinses should suffice. It is important not to use anionic surfactants, which could interfere with subsequent processing.

Many acrylics have a slightly yellow caste which for some shades and end uses might be undesirable. This can be counteracted either by bleaching or by optical whitening or by a combination of both. The normal bleaching agent for acrylic fibers is sodium chlorite, $NaClO_2$, which is used in a pH range of 3.5 to 3.8, maintained with formic or oxalic acids. There are optical whiteners which are stable to acid chlorite bleaches and both treatments
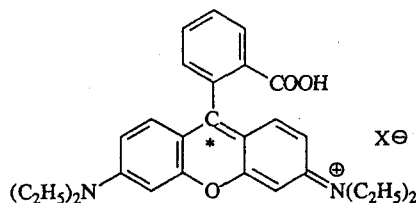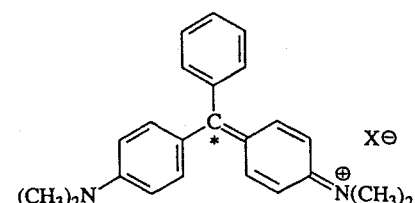
are combinable. Stabilizers should be used to control the chlorine dioxide emissions (e.g., polyphosphates, borax), and corrosion inhibitors (e.g., sodium nitrate) should be present (3). The combined process requires considerable care to ensure the levelness of the optical whitener. Incidentally, the terms optical brightener, optical whitener, fluorescent brightener and fluorescent whitener are synonymous.

Antichlor post treatments after bleaching in baths containing ca. 1 g/L sodium bisulfite and 1 g/L TSPP may not be necessary. But the addition of similarly small amounts of sodium bisulfite or sodium thiosulfate to mix tanks and dyebaths prior to the addition of basic dyes is important. Many basic dyes are very sensitive to variations in the residual hypochlorite content of the water supplied by many small municipalities. Considerable shade fluctuations in pale and pastel acrylic dyeings can result from failing to take the precaution of an antichlor water pretreatment.

Dyebath Chemicals

In addition to antichlors, the primary chemicals present in acrylic dyebaths include sequestrants, wetting agents, pH control chemicals, salts, retarders (levelers) and, of course, the dyes.

● Sequestrants: EDTA, ethylene diamine tetracetic acid and similar products are frequently added as complexing agents to ensure that metal cations will not interfere with the action of any of the other dyes and chemicals present in the dyebath. Only small amounts are required and 0.2% owg will usually suffice.

● Wetting Agents: Whenever hydrophobic fibers are to be dyed it is essential to ensure the goods are thoroughly wet out. Nonionic surfactants have the least likelihood in interfering in ionic processes.

● pH Control Chemicals: Regardless of whether dyeing acrylic fibers with pale shades of disperse dyes or the far more generally applicable basic dyes, a pH range of between 3.5 and 6.0 is most suitable for the hydrolytic stability of the dyes.

As far as the fiber is concerned, unless it contains carboxylic acid groups, introduced with comonomers such as itaconic acid (Table I), the effect of pH on the rate of dyeing is not marked. There is an increase of about 10% per one pH unit in the total amount of dye which will exhaust

onto the fiber. But with carboxylic acid end groups, this increase can be much larger depending on the concentration of the carboxylic acid groups and their pK_a values.

It is convenient that acetic acid is used to assist in dissolving basic dyes because acetic acid in conjunction with sodium acetate can give a buffered dyebath in the pH range 4.5 to 5.5 which is generally used for basic dyeing. Sometimes acetic acid alone is used at 0.5 to 1.0% owg.

● Salts: Those who are familiar with dyeing acid dyes on wool, silk or nylon will already appreciate the use of simple salts such as sodium sulfate as economical retarding agents (2). The sulfate anions compete with dye anions for the fiber cations.

With basic-dyeable acrylic fibers the same effect can be observed, only that now the sodium cations, Na^+, compete with the basic dye cations for the acrylic fiber anions. While the economics are good, the effectiveness is not comparable with that of the organic levelers and retarders which have greater fiber substantivity. A recommended upper limit for anhydrous sodium sulfate use is 2.5 g/L which is equivalent to 10% owg at a liquor ratio of 40:1. At the lower liquor ratios of commercial dyeing practice, the generally used 10% sodium sulfate owg exceeds this upper limit. This is just a reminder to be careful when dealing with concentration or any other parameter which can be expressed in different units.

Levelers or Retarders: General

Basic dye retarders for the anionic acrylic fibers behave in the reverse manner of retarders for wool, silk and nylon. There are still the two types—anionic and cationic—but for anionic acrylic fibers the latter is the more important.

● Cationic Retarders (Leveling Agents): Cationic retarders are usually quaternary ammonium compounds which have a positively charged nitrogen atom surrounded by four substituents. The substituents can include aromatic (benzenoid) groups and long fatty chains.

Cationic retarders have several complementary functions. They effectively swamp out the surface negative potential adjacent to the fiber surfaces (zeta potential). They compete with the basic dyes, first for the anionic charges in the fiber surface layers and then for the negative
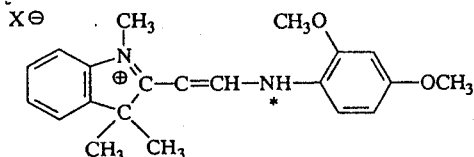
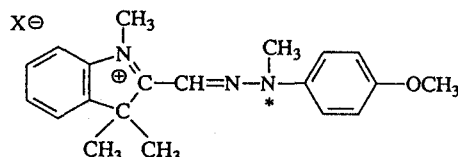Fig. 8. Azacarbocyanine; e.g., C.I. Basic Yellow 11.

Fig. 9. Diazacarbocyanine; e.g., C.I. Basic Yellow 28.

charges within the fiber. All the above taken together can effectively slow down the rate of dyeing.

The retarders can be small molecules of relatively low substantivity and can be applied to the fibers prior to dyeing. These are gradually ejected by incoming dye molecules. Alternatively they can be polymeric molecules with polycationic charges. These are unable to diffuse far into the fiber and they act as a potential barrier to dye cations trying to enter the fibers. More frequently they are of similar substantivity and molecular size to the basic dye molecules themselves and any retarding effect is due to direct competition with the dyes.

● Anionic Retarders (Leveling Agents): Anionic retarders react with basic dye cations in the dyebath to form complex salts. For the complexes to be soluble, the anionic retarders have spare anionic groups on their molecules. This situation can be represented as:

$$Dye^{\oplus} + Retarder^{(1 + n)\ominus}$$
$$\leftrightarrows (Dye \cdot Retarder)^{n\ominus}$$
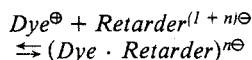
The behavior of these compounds parallels that of the cationic retarders for the anionic acid dyes. In neither case is there competition for the fiber between dye and retarder molecules. The retarding effect is due to there being reduced numbers of dye ions in the bath.

For acrylic fibers, the use of anionic retarders causes the concentration of free dye cations to fall too low for surface saturation of the fiber to occur. The precise position of the equilibrium varies from dye to dye. The result is that dye selections which must be made to ensure dye rate compatibility when using anionic retarders are not the same as those when cationic retarders are used (3).

The subsequent discussion in this chapter centers around the more conventionally used cationic retarders.

Dyeing Cycles

A conventional dyeing procedure is to set the bath with all the chemicals listed except the dyes. The dyeing machine is run for five minutes cold and the liquid dye or predissolved dye is added. The temperature is raised to about 180F (80C) at 3F (1.5C) per minute. From this stage the temperature is raised at only 1F (0.5C) per minute to 205-212F (95-100C) and the dyeing continues at temperature for 60 to 90 minutes.

If dye adds are needed, the temperature is dropped slowly back to below 180F (80C) before continuing. It is important that the temperature drop is slow because the thermoplasticity of acrylic fibers makes crack marks on fabric easy to obtain if cooling is too rapid.

When dyeing is complete, the goods are cooled slowly to ca. 120F (50C), rinsed well, scoured with a little nonionic surfactant (0.5% owg) and a little acetic acid (0.5 to 1% owg glacial acetic acid). The last step is to rinse and apply softener as needed.

Alternative small dyeing variants are used for dyeing the goods in different physical forms (3). But some processes such as constant temperature dyeing are successful mainly with raw stock where uniformity and levelness are not particularly critical.

● Stripping and Leveling: A degree of leveling can be achieved by treatment with a carefully calculated amount of cationic retarder at the boil for one to two hours. For some stripping up to 10% owg of a suitable anionic retarder can be used also at the boil.

For severe or chemical stripping, the goods should be treated with sodium hypochlorite acidified to pH ca. 6 with acetic acid for 30 minutes at the boil. Sodium nitrate (1 to 4 g/L) is required to passivate the stainless steel of the vessel.

Numerical Dyeing Parameters

There are three numerical dyeing parameters which used in conjunction can help the acrylic dyer avoid the problems associated with choosing compatible dyes and help give the greatest probability of satisfactorily uniform dyeings.

The parameters are the combination constant, k; the fiber saturation value, S_F; and the dye saturation factor, f. There is also an equivalent saturation factor, f, which can be determined for many cationic retarders.

● Compatibility: The combination constant, k, is a number from 1 to 5 (half steps are also possible). This number is an indicator of how rapidly any basic dye will dye. The k value of an unknown dye is obtained by first mixing the unknown dye either into each one of five dyebaths containing different yellow (orange) basic dyes, or five dyebaths containing different blue basic dyes. The series selected is the one which contrasts the most strongly with the color of the dye being examined (7).

Each of the five (blue or yellow) standard dyes has a dye rate from 1 to 5, where 1 is the fastest and 5 the slowest. Successive dyeings are made in each bath containing the mixed dyes for short periods of time, taken out and compared for hue. Generally in one of the five dyebaths the hue of the successive mixture dyeings of the standard dye and the dye being examined stays more or less on tone. In such an event, the rates of dyeing of the standard and the dye under examination are essentially the same. They are compatible and have the same k value.

When dyeing mixture shades, dyers should use dyes which, under the dyeing conditions prevailing, have very similar k values; i.e., which are dye rate compatible.

● Fiber Saturation Value: Because there are so many different acrylic and modacrylic fibers, it is important to know how much dye any fiber will hold at saturation, S_F. In order not to get bogged down in physical chemistry units of concentration, such as milliequivalents per kilogram, these S_F values are the percentages of pure C.I. Basic Green 4 crystals (otherwise known as Malachite Green, rmm 400) needed to saturate the particular fiber.

● Fiber saturation values, S_F, normally range from about 1.0 to 4.5. For the chemist, the concentration of anionic end groups is equal to 25 × S_F, meq kg^{-1}.

● Dye Saturation Factor: Each basic dye product has a capacity for saturating anionic groups in the fiber which is based on the equivalent weight of the active color cation and the purity of the product. This capacity is called the dye saturation factor, f.

For any anionic acrylic fiber, the fiber saturation value S_F, is equal to the percentage of any basic dye product required to saturate the fiber, p_s, multiplied by the dye saturation factor for the dye:

$$S_F = p_s \times f \qquad \text{Eq. 1}$$

For pure C.I. Basic Green 4, S_F equals p_s by definition and therefore the value of f for this dye product must equal one (see Eq. 1).

When S_F is known, p_s can be determined by dyeing and f can be derived. Acrylic fiber manufacturers know the S_F values of their fibers; dye manufacturers know the f values of their basic dye products. Values of the same f factor can be derived for many cationic levelers.

In any normal dyeing when there is not enough total dye to saturate the fiber, the product of the percentages any individual dye used and the factor for the dye, $p \times f$,
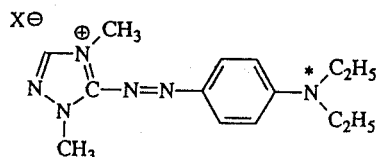
Fig. 10. Diazahemicyanine (Azo); e.g., C.I. Basic Red 22 type.

Fig. 11. Hemicyanine; e.g., C.I. Basic Red 14.

is an indication of that part of the total capacity of the fiber, S_F, satisfied by the particular dye.

This information has two imporant corrollaries:

● The sum of all the $p \times f$ values of all the dyes in a particular recipe should not exceed S_F. Otherwise overdyeing may occur, with the possibility of an unexpected shade of reduced fastness.

● It is possible to calculate the maximum amount of cationic leveling agent which can be used before saturation of the anionic groups in the fiber occurs and the end result becomes uncertain.

If p_1, p_2, p_3 and p_R are the percentages of dyes and retarder in a formulation, and f_1, $f_2 f_3$ and f_R are their saturation factors, then a desirable formulation for a fiber with fiber saturation value S_F is described by the equation:

$$(p_1 \times f_1 + p_2 \times f_2 + p_3 \times f_3 + p_R \times f_R) \leq S_F \quad \text{Eq. 2}$$

This equation clearly parallels dyeing experience in that less cationic leveler is needed (should be used) as the basic dye concentration increases. Familiarity with this simple arithmetic could be valuable to anyone dyeing acrylic fibers.

Cationic-Dyeable Polyester and Nylon

Dyeing suitably modified polyesters with cationic dyes parallels the dyeing of acrylic fibers quite closely. Frequently the source of the polyester fiber anion is the sulfoisophthalic acid monomer; i.e., the polymer contains the fully ionized sulfonate groups at the dyeing pH, ca. 4 to 5. Compared with acrylics, the basic dyes diffuse less rapidly into cationic-dyeable polyester and the chance of unlevelness is not as high even in the presence of carrier. But if carrier must be used it must be removed completely if lightfastness is not to be impaired.

Care must also be taken when dyeing with carrier, or in the presence of disperse dyes, that sufficient nonionic emulsifier is present to prevent coprecipitation of the basic dye by anionic dye dispersing agents and carrier emulsifying agents.

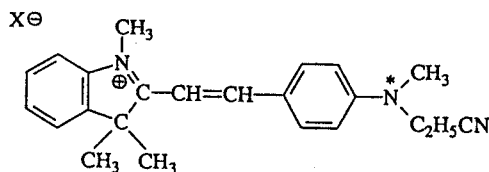The cationic-dyeable nylon has limited use except to give multicolored styling effects when batch dyeing carpets of blended nylons. The principle problem is to ensure that sufficient compatibilizers (nonionic surfactants) are present to ensure that the anionic acid dyes, also present, do not coprecipitate with the basic dye cations.

Basic Dyes: Chemistry and General

The AATCC Buyer's Guide (8) shows that basic dyes hold an important place in the textile dye market. There are 400 products listed under 85 C.I. Names, 42 of which also have published structures and C.I. Numbers. Of these, 31% are blues, 22% are reds and 22% are yellows. There are also oranges, violets and greens. Of the 85, almost half, 32, are offered as liquids.

There is no doubt that as a group basic dyes are the brightest of dyes and their color gamut is enormous. Several are also highly fluorescent.

Although there is no real difficulty in dissolving basic dyes, which are usually pasted with glacial acetic acid followed by hot water and then sieved before adding to the dyebath, they are often sold as liquids. This is for convenience but also because the dust is so extremely highly colored and organic cationic materials are undesirable if inhaled.

The most interesting chemical feature of basic dyes is the variety of their chromophores, some of which are shown in Figs. 2-11. They include anthraquinonoid, azo, triphenylmethane, oxazine, thiazine, xanthene and a variety of products collectively known as polymethines (Figs. 8-11). These latter dyes are relatively recent additions. Many of the more traditional basic dyes have been known for a hundred years and more.

The chemical nomenclature of the polymethine family of dyes and related structures is out of the range of this chapter but is explained in (9). The names of branches on the polymethine family tree are given in the figures.

An important feature of all basic dyes is whether the cations are localized (i.e., confined to a single location) or whether they are delocalized (i.e., can be associated with different atoms of the dye structure). Most are of the later variety and alternate locations for the cationic charges are shown with asterisks (*) in Figs. 4-11. It is those basic dyes with delocalized charges which are responsible for the intense colors associated with the basic dyes.

Review

This concludes the sections of the present work devoted solely to individual dye application categories. The basic dyes have been treated in a manner similar to other dyes. The general mechanism of dyeing has been discussed and it resembles other ion exchange processes quite closely.

Different acrylic and modacrylic fibers have quite a range of concentrations of available anionic charges which lead to very different capacities for dyes at fiber saturation. The capacities are rarely exceeded. The fiber dyes very rapidly above the glass transition temperature and the possibility of unlevelness is of great concern.

Proper selection of retarders or leveling agents when coupled with a knowledge of the following fiber and dye parameters can eliminate many of the dyers' acrylic dyeing concerns: dye combination constants, k, for dye rate compatibility; fiber saturation value, S_F, expressed in nonphysicochemical terms; dye saturation factors, f; as well as the corresponding values for cationic retarders.

Anionic retarders affect the rates of dyeing and change the k values of dyes. They have no saturation factor and are not as widely used as cationic retarders.

Basic dyes can be divided into those with localized and those with delocalized cationic charges, the later being responsible for the intensity of color associated with these dyes. Basic dyes are readily soluble in water and many are available in liquid form. 〇〇〇

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