A Series on Dyeing

Chapter 11/Part 1: Anionic Dyes and Their Application to Ionic Fibers: Dyeing Nylon with Acid Dyes

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

ABSTRACT

The selection of suitable dyes, dyeing procedures and processing chemicals for dyeing nylon are discussed in some detail. The complexity of choices is indicative of both problems to solve and opportunities to exploit.

KEY TERMS

Acid Dyeing Procedures
Acid Dyes
Aftertreatments
Dyeing
Leveling Agents
Metal Complex Acid Dyes
Nylon
Premetallized Dyes
Wool

To justify the present emphasis on nylon in general and carpeting in particular (to be covered in Part 2), it is only necessary to point out that the U.S. fiber industry produces about 3.5 billion pounds of nylon per year. The carpet industry uses well in excess of 2 billion pounds of fiber annually, which goes into about 1.3 billion square yards of carpeting. Of this enormous carpet fiber market about 75% is nylon, divided about evenly between staple and bulked continuous filament (BCF) yarns. All other U.S. markets for nylon put together do not match this one industry for fiber consumption. Other end uses for nylon include hosiery, knitting yarns, lining fabrics, netting, nightwear, parachutes, parkas, rainwear, sewing yarns, shirts and blouses, sleeping bags, socks, sportswear, swimwear, tapes and straps, tracksuits, underwear, uniforms and upholstery fabrics.

Anionic Dyes for Ionic Fibers

With such a large market for nylon, it is to be expected that the marketplace for acid dyes, so dominant for nylon, would also be very large and competitive. This is the case and its complexity is increased not only because of the variety of chemical types of dye used but also because included in the same application category are acid dyes for wool, silk, and leather dyeing. The dyeing of leather, while similar to that of other proteinaceous materials—e.g., wool and silk—will not be considered here.

- Acid Dyes: The AATCC Buyer's Guide (*1*) lists more than 1000 acid dye products under some 360 Colour Index names. About 70 of these C.I. names are for products used almost exclusively by the leather industry. It will surprise nobody that of these 40 are browns and 10 are blacks.

All hues are represented in the acid dye category and there is no difficulty in finding blacks and greens, by contrast with disperse dyes (*2*). The percentage of textile products appearing in the primary hue groups are reds 26%, blues 22% and yellows 17%. The color gamut is extremely broad and if it were not for some problems of fastness, dye compatibility and cost, there would be very few nonfluorescent shades which could not be matched with acid dyes. The reason fiber reactive dyes have such a wide color gamut is that they, too, are based on many of the same acid dye molecular structures. Compare the structure of C.I. Acid Black 1 (Fig. 1) with that of C.I. Reactive Black 5 (*3*). The only differences are the substitutions in Acid Black 1 of masked vinyl sulfone reactive groups,

$$-SO_2-C_2H_4-OSO_3Na,$$

for the nitro group, $-NO_2$, and the hydrogen atom on the benzene ring marked with an asterisk.

Included in with the conventional acid dyes and comprising about 15% of the C.I. names are the 1:1 and 2:1 premetallized dyes. (There seems to be no clear cut convention and the latter dyes may be referred to as 1:2 premetallized dyes.) For clarity some call these dyes metal complex acid dyes. Most of them are co-ordination dye-metal complexes of chromium and some of cobalt by virtue of which they are relatively dull in shade. Some of these, notably the monosulfonated 1:1 premetallized dyes, are not very obviously anionic (*4*).

It should be noted that besides the regular acid dyes and the premetallized dyes (which are a subset of the acid dyes), there are three additional application categories of anionic dyes which are applicable to ionic wool, silk and nylon fibers. Each of these anionic dye categories has a characteristic additional property distinguishing them clearly from acid dyes. They are:

- Chrome Dyes: The property of being able to form dye-metal complexes is the distinguishing feature of chrome dyes. While they comprise about a third of the dyes used for wool and silk worldwide, only a few blacks are used for nylon.
- Reactive Dyes: These generally have acid dye structures, with the added ability to react with electron rich groups such as the cellulosate ion, Cell-O$^-$, and the amino groups in wool, silk and nylon. Specialized advantages will be discussed in Chapter 11, Part 2.
- Direct Dyes: The cellulose substantivity of direct dye anions, coupled with relatively large molecules and a somewhat restricted color range, does not prevent direct dyes from behaving like economical acid dyes. Some are suitable for heavy shades on nylon and others for union dyeing nylon/cotton blends.

Other Dyes for Ionic Fibers

If all these application categories were not enough for dyeing nylon, there are still two more, although they are certainly not anionic.

- Disperse Dyes: These can be used, notably for excellent nylon barré coverage (*5*), but have limited wetfastness and certain anthraquinonoid dyes show poor resistance to facing by atmospheric contaminants (*6*).
- Basic Dyes: Although they can stain wool and silk very heavily, their only use on

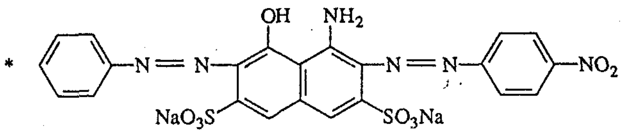

Fig. 1. Disazo acid dye, C.I. Acid Black 1 (cf. C.I. Reactive Black 5).

these fibers is to color silk using an anionic mordant for very bright, economical shades of poor fastness; cf. Perkin's dyeings of the first synthetic dye, Mauveine, ca. 1856. The colored part of basic dye molecules is cationic (+). They can be used to dye specially modified nylon fibers which have a preponderance of anionic carboxylate end groups, $-COO^-$. The main use is to achieve color contrasts in carpeting made from mixtures of nylon yarns with deliberately different dyeabilities and end group concentrations.

In addition to the dye application categories above, it should be pointed out that there is a growing segment of carpet fiber coloration (more predominant in polypropylene than nylon), estimated at ca. 14% in 1988, in which pigments are dispersed throughout the polymer dope prior to extrusion. The coloration process is variously referred to as solution dyeing or dope dyeing, neither of which names is appropriate since no dyes or solutions are involved, or mass pigmentation and producer coloration, both of which names make more sense. Coloration of fibers using pigments will be treated in a later chapter.

Despite the multitude of possible dye application categories for nylon dyeing, acid dyes easily predominate.

Classification of Acid Dyes

Over and over again throughout previous chapters the ways in which the different application categoreis of dyes can be subdivided have been discussed. The same considerations apply with the large family of acid dyes. As on the previous occasions, classification should be based on the chemistry of the dye chromophores. However, such classification is of little use to the dyer. More useful to dyers is classification by dyeing behavior.

Acid Dyes for Wool

Before the introduction of premetallized dyes on nylon fibers, acid dyes were already being subdivided into groups whose names still endure and reflect the wool processing technology for which they were developed. These include the strongly acidic, level dyeing or equalizing acid dyes; the fast acid or half milling dyes; the acid milling dyes; and the neutral dyeing or super milling dyes. The word *milling* refers to the processes by which wool fabrics were converted into felts by mechanical beating treatments in alkaline solutions. Dyes which could be applied to the wool fabric prior to milling and which survived the alkaline treatment were fast to milling.

Wool dyeings are generally carried out at the boil for about an hour. The dyebath conditions necessary for applying these subcategories of acid dyes to wool are:

- Level Dyeing Acid Dyes: 2-4% sulfuric acid owg (pH 2.5-3.5), plus 5-10% owg sodium sulfate for added leveling
- Fast Acid Dyes: 1-3% acetic acid owg (pH 3.5-5.0), plus 5-10% owg sodium sulfate
- Acid Milling Dyes: ca. 4% ammonium sulphate owg, plus acetic acid or ammonia (to pH 5.0-7.5), with the usual addition of 1-2% owg of an organic leveling agent
- Super Milling Dyes: as for acid milling dyes without the acid (pH ca. 7)

It may now be apparent that the level dyeing acid dyes must have intrinsically low substantivity for the wool and have to be induced to dye by lowering the pH, which in turn generates a higher net positive charge associated with the fiber molecules (7). In other words, adding acid increases the substantivity of the dyes for the fiber and for these particular dyes the ionic (coulombic) attraction between their anions and the fiber cations is the predominant form of dye-fiber attachment.

At the other end of the scale, the super milling acid dyes have high substantivity and even in the absence of acid (pH ca. 7, or neutral) they are still strongly attracted to the fiber. For these dyes, the contribution of hydrophobic bonding between dye and fiber is going to be much greater. To underscore this, some of the early super milling acid dyes actually have long hydrocarbon chains included into their dye molecules; e.g., C.I. Acid Blue 138 which has a hydrocarbon chain 12 carbon atoms long, $-C_{12}H_{25}$.

Acid Dyes for Nylon

In general terms, the behavior of the different wool dyeing subgroups of acid dyes were found to be transferable to nylon. Given the differences between all the various nylons 6 and 66, with respect to end group concentrations and the variety of drawing and heatsetting conditions to which they may be subjected, it should be apparent that their behavior towards any dye and the properties of the resultant dyeings will cover a significant range. However, two important general differences between wool and nylon were found:

- Most importantly, the concentration of amino end groups in nylon, and consequently the potential concentration of cationic ammonium groups, is less than 10% that of wool. In practice, this means that if a dye has too many anionic groups per molecule (usually sulfonate groups, $-SO_3^-$) then the number of dye molecules needed to neutralize all the possible cationic charges on the ammonium groups (+) may be small. In fact, it may be too small to permit the dye to build to the heavier depths of shade. For this reason the acid dyes for nylon are largely restricted to those containing only one anionic group, although for some purposes two, and more occasionally three or even four, may be acceptable.
- It was found that the wetfastness of acid dyes on nylon was significantly better than on wool.

About This Series

THIS is the eighteenth installment in this series of papers on dyes and their application. Previous installments have covered the application of anions to nonionic fibers (October 1991), direct dyes (November and December), vat dyes (January and February), sulfur dyes (March and April), reactive dyes (May and June), azoic combinations (August and September), the application of nonionic dyes to fibers (October and November), disperse dyes (December and January) and the application of ionic dyes to ionic fibers (February and March). The series is intended to serve as an introductory text and source book for those who want to expand their understanding of the technology of dyeing and coloration. The author, a frequent contributor to TCC and a member of its Editorial Board, is a professor of textile chemistry at Clemson University.

But what of the 1:1 and 2:1 metal complex acid dyes?

Metal Complex Acid Dyes

The 1:1 premetallized dyes, introduced around 1915, have the unexpected property of being able to migrate and dye wool level at pH's of ca. 2 (or at pH 4 with appropriate dyebath adjuvants) while at the same time giving dyeings of good to very good wetfastness. This still provides them a unique niche for wool dyeing; worldwide they supply ca. 7% of the market. These 1:1 premetallized dyes are useful for dyeing the highly acidic carbonized wool without prior neutralization. They are really the only subgroup of acid dyes which does not appear to obey the general rules of thumb, laid out in the next section. Since nylon is more sensitive to acid hydrolysis than wool, it cannot be dyed at pH 2 without fiber degradation. But several of the 1:1 metal complex dyes can be dyed at pH 4-5 to give level dyeings of very good fastness properties.

The 2:1 premetallized dyes were introduced about 1950. They have large molecules and such high substantivity even at neutral pH's that they require leveling agents and sometimes pHs above 7 to give uniform dyeings of generally very good light and wetfastness. The original members of this subgroup of metal complex acid dyes had limited solubility, but such dyes can be made more soluble by the normal expedient of adding one or sometimes two sulfonate groups. However, the addition causes the substantivity at neutral pH's to be slightly reduced and more acid (lower pH) is needed to acheive the highest levels of exhaustion.

General Characteristics of Acid Dyes

There is a bewildering variety of acid dyes to choose from. They have different molecular structures, chromophores, and numbers and locations of anionic solubilizing groups, to say nothing of fastness properties. Major dye manufacturers have scores of them. Comparing them as a group is like comparing hundreds of apples of different varieties, sizes and degrees of ripeness. However, it is still possible to make useful generalizations about the acid dye (or apple) population.

- The molecular size usually lies in the range from relative molecular mass (rmm) 300-1100. Larger molecules tend to have higher substantivity at neutral pHs; less ability to migrate, level and cover barré; slower rates of diffusion from the surface into the body of the fiber; duller shades; and better wetfastness.
- Increasing the number of ionic solubilizing groups, besides increasing the solubility, decreases the substantivity at any given pH and lowers the pH of optimal exhaustion. It also substantially lowers the upper limit of the concentration of dye, which can be readily exhausted onto the nylon (saturation value). But note: having more than one solubilizing group and lower saturation value does not automatically lead to being unable to achieve dark shades. For example, each molecule of a disazo dye (two azo groups, $-N=N-$) with two sulfonate groups could yield twice the color per molecule of a monoazo monosulfonated dye. So getting half the disazo dye molecules on the fiber would give equal color.
- The largest molecules with the least ionizable groups migrate, level and cover barré least well but have outstanding wetfastness. The smallest molecules, with multiple ionic groups, fall at the other end of the acid dye scale. They require pH 4 or less to exhaust satisfactorily, but migrate and level quite well to give dyeings of, at best, only moderate wetfastness.
- The unique feature of acid dyes is that pH can be used to control both the rate of dyeing (higher for uniformity and levelness) and the extent of dyeing (greater exhaustion at lower pH). With proper procedures, exhaustions of more than 95% can be achieved routinely. Raising the pH above that of the dyeing conditions will tend to strip the dye from the fiber.
- Lightfastness shows little or no relationship to molecular size per se but is related to the unique molecular structure of the individual dye molecules.

Dye Selection

How does anyone set about selecting appropriate acid dyes and a suitable dyeing procedure for a particular type of goods, in particular equipment, for a particular end use? The key word is carefully.

The accumulated experience of the major dye manufacturers is a useful resource for novices and old hands alike. These suppliers have already put together groups of selected acid dyes, from the scores available to them, which are compatible with one another and will satisfy the most diverse technical needs. Such groups may include direct dyes or reactive dyes to increase their versatility. Groups of metal complex dyes may be augmented by selected conventional acid dyes. A recommended procedure may well include a proprietary product—e.g., an amphoteric leveling agent—which could be essential to the compatibility of the dyes in the group (*4*).

For starters, it might be good for a finishing plant to begin with such a group of dyes. Later it might be desirable to substitute one or more dyes of the group for similar dyes from another supplier. But there is no guarantee that substituted dyes will be compatible with the dyeing procedure and proprietary dyeing auxiliaries chosen initially, although similar behavior is more likely if the substituted dyes have the same C.I. names as those being threatened with replacement.

It is important to recognize that selection of an optimal group of dyes and an optimal dyeing procedure for their use cannot be carried out independently.

Table I. Suitable Buffer Solutions for Acid Dyeing

pH	Ammonium or Sodium Acetate g/L	(80%) Acetic Acid mL/L	Monosodium Phosphate g/L	Disodium Phosphate g/L	TSPP[a] g/L
4.0	0.25	1.5[b]			
4.5	0.50	1.0			
5.0	1.00	0.6			
5.5	1.50	0.25			
6.0			2.00	0.50	
6.5			1.50	1.00	
7.0			0.50	1.50	
7.5			0.20	2.00	
8.0		0.42			2.00
8.5		0.30			2.00
9.0		0.20			2.00

[a] $Na_4P_2O_7 \cdot 10\ H_2O$ or tetra sodium pyrophosphate, [b] 1 mL (80%) Acetic Acid = 1.068 grams.

Dye and Dyeing Parameters

Before treating dye and dyeing parameters separately, let us list some of the more important, pH, leveling agents, dye compatibility, time, temperature, liquor ratio, sequestering agents, other auxiliary chemicals, aftertreatments, fastness properties and color. Many of these are interrelated!

- pH: The effect of pH on dyeing rates and extents (% exhaustion) has already been discussed at some length (*4, 7*). Buffered dyebaths are the answer to controlling pH within close tolerances. Where phosphates cannot be tolerated in the effluent, phosphate buffers may have to be foregone in favor of others. Table I shows the pH's which can be achieved with various combinations of simple inorganic chemicals.

One point worth remembering is that ammonium salts hydrolyze to some extent in boiling water with small but significant losses of ammonia and lowering of pH. This is convenient because it means the pH, started high for level dyeing, drops slightly when good exhaustion is needed; i.e., toward the end of the dye cycle. Some companies offer more sophisticated (and expensive) organic materials to achieve a more marked effect.

- Leveling agents: These have also been mentioned previously (*4*). The cationic levelers, or proprietary amphoteric levelers—which are cationic at lower pHs but at higher pHs become anionic—are most interesting, because in the presence of cationic compounds, the rate of dyeing, instead of being controlled by the concentration of dye in the bath, is controlled by the stability (rate of dissociation) of the dye/leveler ionic complex.

This makes it possible to find dyes which exhaust at the same rate in the presence of such levelers but which do not do so in their absence (and vice versa), hence the concern about changing the dyes in formulations using cationic or amphoteric levelers. It is worthwhile to remember that the higher the concentration of dyes in a formulation, the less likely the problem of unlevelness due to poor circulation and too high a rate of dyeing. As a result, the higher the dye concentration (owg), the lower the leveler concentration required.

- Compatibility: There would be no problem of compatibility if all dyeings could be made using single dyes. But since most shades require three different dyes, and sometimes four, it is desirable that dyes in dyebath mixtures are as completely compatible as possible. Ideally this means that not only must the dyes have similar solubility, give stable dyebaths, have similar fastness properties and show similar ability to migrate, but that in a particular optimal dyeing procedure, all the different dye components of the formulation will show equal percentages of exhaustion at any time during the dyeing process. If this ideal can be achieved, there will be no differential strike rate, exhaustion is always on tone—i.e., the hue of the dyed goods will not vary with the time of dyeing—and there will be no differential fading or bleeding in light and washfastness tests.

Dye makers have selected preferred combinations of acid dyes in attempts to meet this difficult goal. Usually they consist of three dyes, known as a trichromie, with several others for augmentation of selected properties such as color gamut. In nylon carpet dyeing, two very widely used trichromies are C.I. Acid Yellow 246 (or 156), Red 361 and Blue 277, and C.I. Acid Yellow 156, Red 266 and Blue 324. But there are other suitable colors. The dust of C.I. Acid Yellow 156 has been found to be toxic if inhaled. Fortunately for carpet dyers, most acid dyes are sold and used in liquid form.

For automotive carpeting, where the highest standards of lightfastness are essential, the selection of suitable dyes comes primarily from the 2:1 premetallized dyes (see Part 2).

- Time and temperature: These are inseparable. The time it takes to raise the dyebath to the dyeing temperature and achieve both exhaustion and uniform penetration of dye into the heart of the fibers depends on both the rate of rise of temperature and the dyeing temperature used. Dyeing temperatures can range from ca. 87C (190F) to 110C (230F). But if the dyeings are carried out under pressure, care must be taken that no air is present because oxygen can degrade the nylon.
- Liquor ratio: The benefits of short liquor ratios are in energy savings and in efficient use of chemicals. However, the optimal liquor: goods ratio is usually determined in large measure by the dyeing equipment and the physical form of the goods being dyed.
- Sequestering agents: Sometimes known as sequestrants, these chemicals form stable complexes with unwanted metal ions in process water, such as the calcium, magnesium, iron (Fe^{2+}, Fe^{3+}) and copper (Cu^{2+}) ions. These metal ions can cause considerable shade change and dulling, particularly with dyeings of certain acid dyes such as C.I. Acid Red 73. They even cause some premetallized dyes to change color, no doubt by partially exchanging the metal in the complex for iron or copper; e.g., C.I. Acid Orange 60.

Great care should be exercised when considering the use of sequestrants (such as EDTA or sodium hexametaphosphate) with metal complex acid dyes, for they tend to demetallize the dyes with consequent shade changes.

- Wetting and deaerating agents: The most important consideration when such agents must be used is that they do not interfere with the other auxillary products or dyes already included in the bath; for example, amphoteric or cationic leveling agents used with 2:1 premetallized dyes or anionic levelers used primarily with conventional acid dyes.

The wetting agents are usually selected nonionic surfactants or the sodium salt of dioctylsulfosuccinate (DOSS) which, although it is anionic, has virtually no substantivity and is not a leveling agent.

- Aftertreatments: In the early days of nylon dyeing, it was discovered that aftertreatment with tannic acid followed by a further treatment with tartar emetic (potassium antimonyl tartrate) improved the wetfastness of acid dyes on nylon. It was thought that the combination formed a complex insoluble outer layer in the fiber surface through which acid dyes could not diffuse, either in or out of the fiber.

After dyeing and rinsing off thoroughly, the goods are treated first in a bath containing 2% owg tannic acid, 2% owg formic acid (85%), the temperature is raised to ca. 160F (70C) for nylon 6 or ca. 195F (90C) for nylon 66 and the treatment continued for about 30 minutes. About 2% owg tartar emetic is added and treatment continued for a further 20 minutes.

The resultant backtanned goods are noticeably stiffer and slightly yellower, but the dyeings are faster to washing. Because of the added yellowness, there is normally a restriction of the full backtanning process to heavier dull shades. Alternatives were sought and a range of materials were found which were based on phenols, naphthols or diphenyl sulfones, sulfonated and condensed with formaldehyde. These colorless polymeric materials were applied and behaved rather like tannic acid. Consequently they became known as syntans, or synthetic tanning agents. They do not give quite the improvement in wetfastness that tannic acid/tartar emetic does, but there is no yellowing of the goods during the treatment. However, they were also found to have a number of other properties. One of these properties, while not entirely unexpected, has been exploited heavily in the manufacture of nylon carpets since late 1986, to provide resistance to staining by acid dyes in artificially colored fruit drinks (see Part 2).

- Photostabilizers: These are products which protect both nylon fibers and the dyes with which they are colored from degradation due to exposure to near UV and visible radiation and thereby improve lightfastness. They are particularly important for automotive upholstery and carpet fabrics. Photostabilizers will be discussed further in Part 2.

However, while on the subject of lightfastness, it is important to note that the lightfastness and ozonefastness of dyes on nylon 6 and 66 are very sensitive to all kinds of residual chemicals on the fiber. Any chemical auxiliary being used for nylon should be carefully screened with this in mind.

Typical Dyeing Procedures

Nylon woven fabrics can be dyed in open width on beams and jigs if they are prone to creasing, or in rope form in becks and jets. Typical beck dyeing procedures are given below.

- Acid Leveling Dyes: C.I. Acid Yellow 49, Red 337 and Blue 40 can be taken as examples. This trichromie of acid leveling dyes might be very suitable for dyeing in combination to give fashionable shades with good lightfastness on goods which might otherwise show barré. However, the resultant dyeings would definitely require either a full backtanning aftertreatment or treatment with a syntan to improve the wetfastness *(see above)*. The dyeings require the use of an appropriate anionic leveling agent. Two approaches could be used.

In normal circumstances, the bath should be set with 1-2% anionic leveling agent and either acetic acid or a buffer to pH 4.5-5.5 (Table I). The paler the shade the higher the starting pH, since in light shades the rate of dyeing is intrinsically faster in any given set of conditions. The goods are pretreated in the bath with good circulation for 10-20 minutes at 105F (40C). After the predissolved dye is added, the temperature is raised to 212F (100C) at about 4F (2C) per minute. Dyeing is conducted at that temperature for ca. 60 minutes.

Alternatively, for better coverage of barré, the anionic leveler can be exhausted onto the fiber (under similar conditions to the dye in the previous paragraph) for 15-20 minutes at 212F (100C), followed by cooling back to 120F (50C) and adding the dissolved dye and proceeding as before. This somewhat laborious sequence is designed to achieve maximum coverage of fiber variations.

- 2:1 Metal Complex Dyes: Good trichromatic (if dull) combinations might be selected from C.I. Acid Yellow 162, Red 251 (or 226) and Blue 171 augmented by C.I. Acid Black 132, where good wash and lightfastness is necessary, as in automotive fabrics. The combination would not be very forgiving of barré.

The bath is adjusted to about 90F (32C) with a suitable buffer (see Table I) to adjust to pH 6-6.5. Again, the paler the shade the higher the starting pH. Frequently, ca. 3-4% owg ammonium sulfate is used and the pH adjusted if necessary. The goods are then run 5-10 minutes and a suitable proprietary amphoteric (cationic) carrier is added. The amount may be varied with the depth of shade from 0.5-1-0% owg with the heavier depths requiring the lower concentrations of leveler. The goods are then circulated a further 5-10 minutes, the predissolved premetallized dyes are added and the liquor circulated again for 5-10 minutes.

The temperature is raised at 2F (1C) per minute to 212F (100C), but the temperature rise may be interrupted for 10-20 minutes if there is a critical dyeing temperature for the particular goods, which often occurs in the 140-160F (60-70C) region.

After dyeing for 30-45 minutes, the bath is cooled to 160F (70C) for sampling and the shade is subsequently rinsed and scoured. Post-treatment to improve the wetfastness should not be necessary.

A very thorough treatment of dyeing both nylon and polyurethanes is given in Ref. 8 comprising ca. 50,000 words and 77 references.

Leveling and Stripping

If shaded fabrics need repair, the procedure is to add up to 1% owg additional leveling agent, adjust the pH to 8-8.5, raise to the boil and boil for ca. 30 minutes. Depending on the substantivity of the dyes being used, a greater or lesser amount of the dye will be stripped into the bath and this dye can be re-exhausted onto the goods simply by lowering the pH to an appropriate value and redyeing.

Chemical stripping is usually effected at pH ca. 4. For example, at about 195F (90C) 4% owg sodium sulfoxalate formaldehyde is added and the temperature raised to near the boil for 15 minutes. In some circumstances, higher temperatures (220F) and other reducing agents are used. A mild post-treatment with a little sequestrant—ca. 0.3% owg at 140F (60C)—completes the process. However, some acid dyes are hard to strip completely.

More About Anionic Levelers

Some optimized ionic dyeing processes for both anionic and cationic fibers are based on the following simple principles and some associated arithmetic:

- That dyes can be selected for compatibility based on their individual rates of dyeing on the substrate (in this case, some type of polyamide fiber) provided they are of similar physical types (e.g., monosulfonated acid dyes)
- That dyes and levelers of the same ionic type (anionic in this case) can be categorized on the basis of the concentration required for them to neutralize or saturate the oppositely charged groups in the fiber ($-NH_3^{\oplus}$)
- That the greatest degree of leveling is achieved when the sum of the concentrations of the dyes and the leveler in the formulation are just sufficient to equal the saturation value of the fiber.

The corollaries are that too much leveler would cause blocking of dyes in the formulation from dyeing the fiber, but to do so in a manner which leaves the dyeings on shade but light in depth. The lower the combined concentration of dyes, the higher the permissible concentration of leveler.

The above principles will be expanded in Chapter 13 in the consideration of basic (cationic) dyes and cationic levelers on the anionic acrylic and cationic dyeable polyester fibers.

Review

The variables which play a role in determining the correct selection of dyes, dyeing procedures, auxiliary chemicals, particularly leveling agents and dye aftertreatments, have been discussed. All of these depend on the nature of the nylon being processed, the depth of shade being dyed and the fastness properties expected of the finished goods. The author is reminded of a Total Quality Management poster showing an elderly couple submerged up to their necks in a steaming hot Jacuzzi tub. The caption read: "Opportunities and Problems!"

The rewards are there for the company which will invest the time and effort to master, rationalize and optimize its nylon dyeing procedures and, by so doing, gain a cost and quality advantage over its competitors. ꝏ

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