AATCC WORKSHOP

The Basics of Dyeing and Finishing of Natural and Synthetic Fibers

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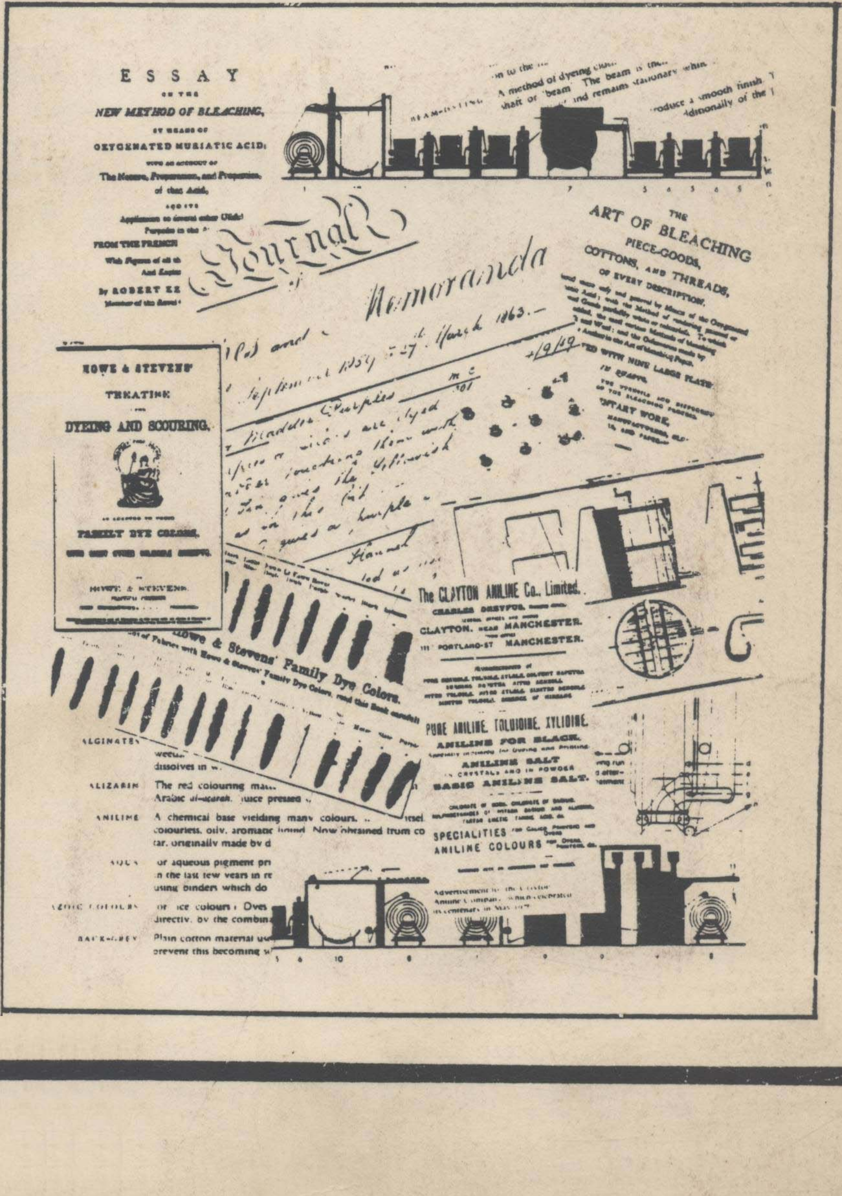

Papers Contributed By

J. Richard Aspland
Clemson University

Michel A. Herlant
Crompton & Knowles

Patrick L. Moriarty
Eastman Chemical
Products, Inc.

J. Lee Rush
Allied Corporation

G. Robert Turner
TEXTILE CHEMIST AND COLORIST

Jesse G. Camp
Gaston County Dyeing
Machine Company

Rob L. Stone
Cotton Inc.

Bernard F. North
Sun Chemical Corporation

C. Hugh Patrick, Jr.
Pat-Chem, Inc.

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Dyeing Primer

A Series of Short Papers on the Fundamentals of Dyeing

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Dyeing Primer: Part I

What Are Dyes? What Is Dyeing?

By J. RICHARD ASPLAND, Reeves Brothers Inc., Charlotte, N. C.

HIGHLY colored substances, known logically enough as colorants, can be used to impart color to an infinite variety of materials described technically as substrates. Colorants can be subdivided into dyes, which are soluble in the medium in which they are applied, and pigments, which are insoluble in the application medium. Substrates can be subdivided into textile and nontextile, or fibrous and nonfibrous materials.

The series of short primer papers, of which this is the first, will deal with the application of dyes to fibrous, textile substrates.

It should be emphasized from the start that the three major variables involved in dyeing are the physical and chemical natures of the dye, the substrate and the application medium. To understand textile dyeing, one must be able to appreciate the various interactions possible between particular types of dyes and different types of fibers in the presence of the application medium, which is usually water. The resistance of dyeings to color change or loss (fastness) depends on the same variables.

ABSTRACT

This is the first of a series of 12 short papers prepared at the request of the AATCC Publications Committee to serve as primers on the coloration of textiles for those who have had no formal introduction to the subject. General information is presented here to introduce the subsequent papers, which will deal with more specific dyeing topics.

KEY TERMS

Colorants
Dyes
Dyeing
Primer

Dyeing is undoubtedly a mature technology, but that does not mean it is free from problems. Today's difficulties revolve around the multiplicity of textile fibers, the number of dye application categories and the variety of products within each category, the spectrum of different blended yarns and fabrics and the plethora of fastness, quality control and economic requirements for the resultant dyed goods. In these circumstances, a better understanding of the fundamentals of dyes and dyeing cannot come amiss.

Historical Background

There is evidence that the art of dyeing has been known for about 50 centuries, probably originating in India or China not later than 2500 BC. Dyes capable of giving a full range of hues on linen were known by 1400 BC; mixing yellow, red and blue dyes to give secondary and tertiary shades on fabrics was practiced before 150 AD; and the art of Oriental carpet making, with its splendid variety of colors and designs, was approaching its peak by 1500 AD.

Natural Dyes

From earliest times until the middle of the 19th century, the dyes used were mostly of vegetable origin, and their use posed many problems. Sources of supply were unreliable and standardization was nonexistent. Many of the dyes did not have a strong attraction for the fibers (substantivity). This was overcome by first treating the fibers—often using complicated recipes—with solutions of aluminum, copper, iron and, after 1850, chromium salts. The process was known as mordanting. During subsequent dyeing, the metal derivatives (or mordants) which are deposited in the fiber react with the dye to give water insoluble complexes whose color often depends on the nature of the mordant. The yarns from which antique Oriental carpets were woven were mordant dye, but much of the charm of these carpets lies in the subtle, unintentional variations of hue within areas of the pattern of similar overall color.

Natural indigo, which occurs in a chemically combined state in several plants, required a long fermentation process to yield the dye in a pale yellow water soluble form. This form has some substantivity for cotton and wool and the blue color is restored by exposure of the dyed goods to the air.

Natural dyes do not give very bright colors compared with those of synthetic dyes, and they have become progressively less and less important since the advent of synthetic dyes in the mid-19th century. Today, logwood black is the only natural dye widely used. It is a romantic illusion that natural dyes produced dyeings with technical properties unattainable nowadays.

Synthetic Dyes

With his discovery in 1856 of the purple dye mauveine, William Henry Perkin initiated not only the manufacture of synthetic dyes and pigments but also the whole synthetic organic chemical industry.

Azo dyes were discovered in 1862, based on the work of Peter Griess, and are the largest single chemical category of dyes. In 1884 the first direct cotton dye, Congo Red, was discovered. It was the first synthetic dye with sufficient substantivity for cellulose not to require a mordant. Azoic dyes date from 1911 and disperse dyes, for what were then the new man-made acetate fibers, followed in 1923. Disperse dyes for acetate are azo and anthraquinone derivatives and are very similar chemically to the disperse dyes used for polyester today. The rediscovery and realization of the potential of phthalocyanine blues in 1936 introduced a new brilliancy into turquoise and green-blue pigments and dyes of all application classes. The first fiber reactive dyes capable of forming covalent linkages with the fiber were marketed in 1956, just 100 years after Perkin's initial breakthrough.

What started in a home laboratory has now become a worldwide industry producing about 7000 different dyes. In

1977, shipments of organic pigments and dyes by U.S. manufacturers were valued at more than $1 billion, and the U.S. textile industry used about $500 million worth of dyes (*1*).

Dye And Pigment Manufacture

Traditionally, synthetic dyes were known as coal tar dyes because the aromatic organic raw materials for dye manufacture, all of which contain six-membered ring structures of carbon atoms, were derived from coal tar. Major raw materials are benzene, toluene, xylenes, naphthalene and anthracene. In the U.S. these materials are supplied largely by the petrochemical industry.

Dye precursors known as intermediates are derived from the raw materials. To convert a raw material to an intermediate usually involves one or more general chemical reactions known as unit processes. These include nitration, sulfonation, halogenation, reduction, amination, hydroxylation and oxidation.

The conversion of these intermediates into dyes and pigments may require further use of unit processes. For example, most azo dyes and pigments are made by the diazotization of a primary aromatic amine in ice-cold acid solution using nitrous acid. The diazonium salt formed is then coupled with another aromatic amine, a naphthol or a phenol to produce an azo colorant.

It is very important to recognize that, despite the overall magnitude of the dye and pigment manufacturing industry, the making of most dyes is still a multistage batch process.

The total annual production of any particular dye might not amount to more than ten tons. Add to this that synthetic dyes and pigments belong to 29 different chemical structure categories and more than a dozen different application categories, and that even one of the simpler dyes may require eight to ten unit processes to convert the raw material through the intermediates to the finished product. These considerations effectively rule out continuous manufacturing methods in most cases.

The multistage nature of dye manufacture also reflects on the nature of the chemical reactions involved. Any reaction suitable for a dye or intermediate manufacturing process must be relatively clean, straight-forward and give the desired product in very good yield. The diazotization and coupling reactions (from which azo dyes are derived) can frequently be carried out with yields of better than 95%, and it is a simple matter of permutations and combinations to show that large numbers of different dyes can be generated from relatively few amines and coupling components.

Nowadays, azo dyes are becoming even more prominent because anthraquinone dyes, the second largest chemical group of dyes, have become very expensive, and their manufacture presents various environmental and technical problems.

Properties Of Dyes And Pigments

All dyes and pigments must have a number of properties to be useful. They must be highly colored and yield colored goods with fastness; i.e., resistance to shade changes or color loss in subsequent treatments (such as resin finishing) or in use (such as exposure to light or washing). Frequently a compromise must be reached between the cost of attaining a particular color of goods and the fastness properties of those goods. As a rough guide, the higher the cost of the dyeing, the better the fastness properties. Commercial products must be standardized to give acceptably consistent shades, depths of shade and other physical properties, and often contain as little as 10-20% of actual color.

Dyes must be soluble, molecularly dispersible or capable of being made soluble in the medium in which they are applied. Water is almost always the application medium. Substituent groups which confer water solubility on dye molecules are of two types, those which are an integral part of the dye molecule, and those which are introduced temporarily to be removed during the dyeing process.

Integral solubilizing groups in dyes include: sodium sulfonate groups, which are dissociated in aqueous solution into colored, negatively-charged, dye-sulfonate anions and colorless sodium ions (acid, direct and fiber reactive dyes); quaternary amine chlorides, which are dissociated into colored, positively-charged, quaternary amino dye cations and colorless chloride ions (basic or cationic dyes); hydroxy, amino and substituted amino groups, which are not ionic and do not in general dissociate under normal dyebath conditions, but do confer some solubility (disperse dyes).

Temporary solubilizing groups include: sodium phenates, which exist in strongly alkaline solutions as negatively-charged dye anions and sodium ions (reduced vat dyes and azoic coupling components); sodium thio-phenates which exist in alkaline solutions as negatively-charged dye anions and sodium ions (reduced or liquid sulfur dyes).

Dyes must also be capable of diffusing into the fibers under the conditions of dyeing. The diffused dye must be retained by the fiber. This can occur in three different ways:

- The dye may be substantive to the fiber, in which case it becomes physically bound to the fiber by one or more of: ionic forces, hydrogen-bonding, or Van der Waals' forces. Ionic forces are the simplest to understand, being the attraction between positively and negatively-charged ions, one on the dye and the other on the fiber. Hydrogen-bonding is associated with the sharing of electrons, in this case between dye and fiber molecules. Van de Waals' forces are attractions between atoms or molecules when placed in very close proximity.
- The dye may react to form a covalent chemical bond with the fibers.
- Temporary solubilizing groups may be removed, leaving the dye stranded and insoluble within the fibrous substrate.

Pigments must be insoluble in the medium in which they are applied. But they also must meet a variety of physical criteria respecting their particle size and flow properties when incorporated in the application medium.

Properties Of Fibers

Fibers are the fundamental textile raw materials. They can be natural (wool, cotton, silk), regenerated (viscose, acetate) or completely synthetic (nylon, polyester, acrylic), and they are all comprised of long chain polymer molecules oriented more or less parallel to the fiber axis.

In crystalline regions the polymer molecules are packed very closely and regularly; in amorphous regions the packing is looser and more random.

During dyeing, dye molecules must somehow diffuse from the external phase, usually aqueous, and into the fibers. Since the crystalline regions are very difficult to penetrate (even by water), the ratio of crystalline to amorphous regions is very important to the dyeability of fibers. The more perfectly aligned the polymer chains are along the fiber axis, the higher is the fiber orientation and the less readily is the fiber penetrated by dye. Fibers such as cotton which absorb water readily and swell appreciably are known as hydrophilic; fibers which absorb water only with some difficulty and which swell very little are known as hydrophobic; for example, polyester.

The ionic character of fibers strongly influences their dyeability. If the polymer chains in the fiber either carry or can be induced to carry ionic charges, by correct selection of the dyebath conditions they will be potentially able to interact with oppositely charged colored ions. For example, the polymer chains in wool, silk and nylon can be induced to carry positive charges in acid solutions. This gives them the potential for attracting the colored dye anions from direct, acid and fiber reactive dyes. Conversely, carboxyl groups in nylon under alkaline conditions may ionize to give carboxylate anions which would tend to repel dye anions.

Little of general interest is known about the nonionic interactions between individual dyes and fiber molecules, though an increase in dye molecular weight often results in increased substantivity.

Summary

We have taken a brief look at the history and manufacture of dyes and pigments, and at some of those properties of dyes and fibers which influence dyeing.

Subsequent papers in this series will deal with specific application classes of dyes and the fibers for which they are used, and also with the reasoning behind the choice of dyeing conditions for particular dye-fiber combinations.

It is advisable, nevertheless, not to lose sight of the broad general principles on which dyeing rests, because there are many yarns and fabrics which contain blends of fibers with markedly different dyeing properties, and they will require the proper selection and use of mixtures of dyes from different application classes.

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Dyeing Primer: Part 2

Dyeing With Acid Dyes

By J. LEE RUSH, Allied Chemical Corp., Petersburg, Va.

THE name "acid dye" is derived from the dyeing process. The dyes are applied to wool, silk and polyamides in the presence of an organic or inorganic acid and, hence, are called acid dyes. The term acid dye denotes a large group of anionic dyes with relatively low molecular weights that carry from one to three sulfonic acid groups. Chemically, acid dyes belong to such various subclasses as nitro, nitroso, monoazo, diazo, triphenyl methane, xanthene, azine, quinoline, ketone-imine and anthraquinone. Like direct dyes, acid dyes may be represented as $R\text{-}SO_3Na$ and in this respect, they resemble each other. When dissolved in water, they produce colored anions (RSO_3^-) and colorless sodium cations (Na^+).

Classification of Acid Dyes

One method of classifying acid dyes is that of dividing them into three groups according to their application and wetfastness properties: (1) leveling dyes, (2) milling dyes, and (3) super milling dyes. This classification was originally devised for wool dyeing, as the term "milling" indicates, and its application to polyamide fibers must be made with caution.

Leveling Dyes

As a class, the leveling acid dyes level well, and their lightfastness is generally good. Their fastness to wet treatments, however, is not entirely satisfactory. Leveling dyes for wool have low molecular weights and usually require a highly acidic dyebath for good exhaustion. On nylon, leveling dyes are of higher molecular weight and they are applied at a neutral or weakly acidic pH.

Milling Dyes

Milling acid dyes have better washing fastness than the leveling acid dyes but generally the shades lack brightness and the good leveling power of the leveling type of acid dyes. They are generally used where good washfastness is the main consideration. The dyes are in general of higher molecular weight than the wool leveling dyes. They are generally applied from a weakly acid liquor in the pH range of 5.2 to 6.2; and they are customarily applied with acetic acid. Milling is an essential process in the production of felts in which woolen fabrics are shrunk by treatment with a combination of concentrated soap solution and mechanical action. Any dye which can withstand this process has to have superior wetfastness.

Super Milling Dyes

Super milling acid dyes are applied from neutral solutions. They are not level dyeing, and their application requires considerable care because of their comparatively high molecular weights. They are often referred to as the fast acid dyes or acid milling types because originally they were used in wool fabrics which were to be subjected to severe wet treatments in processing ("milling") to improve the fabric density and hand. Also called neutral dyeing acid dyes, they possess good light and wet fastness.

As a consequence of the above facts, a blocking effect is observed in practical dyeings. If a polyamide fiber is dyed with a mixture of monosulfonic and trisulfonic dye, it is generally the monobasic dye which will be taken up and it will have a blocking effect on the polybasic dye.

Metal Complex Dyes

Metal complex dyes, which are the reaction products of chromium or cobalt ions and selected dyes, are usually considered with acid dyes. The 1:1 metal complex dye has one equivalent of metal for each equivalent of dye. It always carries one or two sulfonic groups, contributed by the reagent dye and it is applied from strongly acid solution. The 1:2 metal complex dyes contain one equivalent of metal combined with two equivalents of dye, and in this case, the dyes selected do not normally contain sulfonic acid solubilizing groups. After the 1:2 complexing reaction the new dye-metal complex has an overall negative charge—i.e., is anionic—but this charge is not localized and is distributed over the dye molecule. These dyes are not as bright as a true acid dye, but they are very stable and give dyeings with excellent fastness to light and washing.

Dye-Fiber Bonds

All polyamide fibers have the following groups:

terminal amino groups $—NH_2$
terminal carboxyl groups $—COOH$
and imido groups along the chain $—NH—$.

This can be simplified to:

$$H_2N—NH—COOH$$

ABSTRACT

The author discusses how acid dyeing originated, the characteristics of acid dyes, and what fibers are dyed with acid dyes. Acid dye classes are given together with a typical method of how the dyes are applied. Problems in applying acid dyes uniformly and what can be done to correct them are described. Methods for stripping acid dyes and methods for increasing their wetfastness are discussed. A brief discussion of dyeing kinetics is also given.

KEY TERMS

Acid Dyes
Dyeing
Leveling Dyes
Milling Dyes
Polyamide Fibers
Silk
Stripping
Super Milling Dyes
Wool

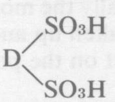
This is the second of a series of 12 short papers on the fundamentals of dyeing. The series is intended for those who have had no formal introduction to the subject. Basically it will cover the application of various classes of dyes to various types of fibers. The series began last month and will appear monthly until it is concluded. (For a list of the topics to be covered, see page 25 of TCC for January.)

These groups react as follows at different pH values:

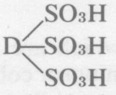
$\mathrm{H_2N{-}NH{-}COOH}$
(neutral)
$\rightarrow\mathrm{NH_3^+{-}NH{-}COO^-}$
(weakly acid)
$\rightarrow\mathrm{NH_3^+{-}COOH}$
(very strongly acid)

These positively charged groups in the polyamide can take up anions by the formation of salt-like compounds. Acid dyes, direct, chrome, soluble disperse and reactive dyes all contain solubilizing groups or anionic sulfonic acid groups ($\mathrm{{-}SO_3H}$). If the dyestuff molecule is called "D", the different types of dyes can be represented as follows:

$\mathrm{D{-}SO_3H}$
(monosulfonic acid)



(disulfonic acid)



(trisulfonic acid)

These dyes dissociate to positively and negatively charged particles:

$\mathrm{DSO_3H \rightleftarrows H^+ + DSO_3^-}$

Since there is only one terminal amino group per polyamide chain, the number of sites for salt formation in a polyamide filament is limited. At a pH higher than about 2.0, acid wool dyes can be taken up by polyamide fibers up to the saturation value, and if all terminal $\mathrm{NH_2}$ groups are occupied, no more dye can be bound in this manner.

The trisulfonic acids have a lower saturation value than the disulfonic acids, and disulfonic acids lower than monosulfonic acids.

As a consequence, the so-called blocking effect is observed in practice. When a polyamide fiber is dyed with a mixture of monosulfonic and trisulfonic dye, it is generally the monobasic dye which will be taken up and it will have a blocking effect on the polybasic dye.

Being a protein fiber, wool holds dyes similar to polyamides and forms salt linkages. The wool fiber contains salt links of the type:

$\mathrm{^-OOC{-}W{-}NH_3^+}$

These are electrically neutral. The presence of hydrogen ions leaves a net positive charge:

$\mathrm{^-OOC{-}W{-}NH_3^+ + H^+}$
$\rightarrow\mathrm{HOOC{-}W{-}NH_3^+}$

This system is now capable of attracting dye anions:

$\mathrm{HOOC{-}W{-}NH_3^+ + D^-}$
$\rightarrow\mathrm{HOOC{-}W{-}NH_3D}$

Preparation Of Substrates

Silk and wool must be scoured thoroughly before dyeing to remove natural gums and oils. When dyeing pale shades on wool, it is often necessary to bleach with hydrogen peroxide before dyeing. Polyamides (nylon) are usually not prescoured before dyeing. Sometimes, when tints have been applied to polyamides for segregation during fiber processing, it is necessary to give the fiber an alkaline sodium perborate scour to get satisfactory pale shades.

Typical Dyeing Procedures For Leveling Acid Dyes

Polyamide

The liquor is made up with 1% acetic acid and 2% ammonium acetate. 1-2% leveling agent and 0.25% sequestrant are added. The goods are entered at 40C (104F) at a liquor ratio of 30:1 and run 10 to 20 minutes before the predissolved acid dyes are added. The liquor is raised to the boil over a period of 45 minutes and maintained there for 45 minutes to 1 hour, when dyeing should be complete. With level dyeing dyes, additions can be made at the boil. With less level dyeing colors, the bath should be cooled to 71C (160F) before additions are made.

Wool

Set the dyebath cold with 10% sodium sulfate, 3% sulfuric acid. The predissolved acid dyes are then added. Enter the fabric into the 50:1 liquor and raise the bath to the boil in 20 minutes. Continue boiling for 1 hour and then rinse and dry.

Purpose Of The Chemicals

The acetic acid and ammonium acetate are used to control pH and to make sure the pH ends up on the acid side. The leveling agent is used to retard the strike of the dye and to promote leveling. There are two main types of leveling agents used: (1) anionic, which diffuses into the fiber more rapidly but is less firmly held by the fiber and is gradually replaced by the dye; and (2) cationic, which forms a complex with the dye in solution and breaks up only at higher temperatures, allowing the dye to go onto the fiber slowly. The sequestering agent complexes with unwanted metal ions in water to prevent them from contaminating the dyes in solution.

How The Dye Is Applied

The dye becomes associated with the substrate in three principal stages: (1) movement of dye (in solution) with the flow of the dyebath and diffusion of the dye through the aqueous dyebath to the fiber surface; (2) adsorption of dye on the outer surface of the fiber; and (3) diffusion of dye inside the fiber from the surface towards the center.

The adsorption process is generally believed to be so much more rapid than either diffusion step that it is regarded as instantaneous. Of the two steps involving diffusion, the diffusion into the fiber is much slower than that from the aqueous solution, provided the dye solution is adequately circulated through the fabric. In the early stages of dyeing, the dye is distributed nonuniformly through the fiber with a high concentration on the surface and a low concentration inside the fiber. The existence of such a concentration gradient causes dye to diffuse towards the center of the fiber at a rate proportional to this gradient.

The rate of sorption of acid dyes is influenced greatly by temperature. There is very little transfer of the dye to the fiber below 39C (102F). From this temperature upwards, the rate of adsorption increases. Each dye has its own range at which adsorption is at a maximum, and the characteristics of the particular fiber are also important.

It is important in bulk dyeing that the rate of temperature rise is slow over the critical phase. The molecularly dispersed acid dyes give level shades because they migrate in a boiling liquor. The molecules attached to the fiber constantly unattached at one site and refix at another. This perpetual movement of the dye within the fibers—and between the fibers—causes a more or less complete randomization to take place, so that the distribution is uniform. This phenomenon, known as migration or leveling, is a factor which must be taken into account when selecting dyes.

Improving Wetfastness Of Acid Dyeings

Significant improvement in the wetfastness of acid dyeings can be obtained by using 1-3% of a fixing agent such as Erional NW (Ciba-Geigy) or Mesitol NBS (Mobay) in an acid medium as an aftertreatment. This treatment causes some slight change in shade and a stiffening of the fabric hand. A more permanent method is through the use of aftertreating with formic acid, tannic acid and tartar emetic. This treatment often changes the original shade significantly and impairs lightfastness if the tannic acid quality is not excellent.

Stripping Of Acid Dyes

Occasionally, when fabrics are hopelessly off-shade or unlevel, it is necessary to remove the dye by a process called stripping. In stripping, the dye is destroyed either by oxidation or reduction. A typical oxidation strip for wool is done with 5% potassium dichromate and 10% sulfuric acid. The normal oxidation method for nylon is with sodium perborate and ammonia. A reduction strip is accomplished on nylon with 3% sodium formaldehydesulphoxylate and 1% acetic acid or sodium hydrosulfite and soda ash. Once the dye is removed, the fabric can be redyed to the desired shade.

Special Problems

When dyeing wool, it has been found that even though the distribution of the dye liquor is perfect, it is still possible to obtain large or small scale unevenness in different areas of the cloth, due to different affinities for the dye or different dyeing rates. This unevenness in wool dyeings has led to the term "skittery dyeings." Skittery dyeings have been found to contain four types of fiber: (1) undyed, (2) partly dyed or ring dyed, (3) completely but lightly dyed, and (4) completely and heavily dyed. It has been suggested that a possible reason for the different dye behavior of wool fibers is the exposure of the tips of the wool fiber to weather, when still on the sheep, causing degradation by sunlight, air, rain or friction, whereas the wool next to the skin of the sheep is protected. In addition, wool from different parts of the sheep's body can suffer varying amounts of degradation. Another reason for skittery dyeing could be fibers from different sheep. They very well might differ in diameter, and hence in surface area.

Many of the dyes commonly used to dye polyamides can form streaky or barré dyeings. This can be caused by a number of fiber related factors: (1) difference in dye affinity from different spinning batches, (2) optical differences due to denier variation, (3) optical differences due to delustrant content, (4) variation in the number of terminal amino groups, (5) differences in the rate of dyeing due to varying degrees of crystallization or differences in fiber stretching, and (6) variations in twist setting temperatures. These are all legitimate sources of uneven dyeings pointed out in the literature; however, with the improvements made in the manufacture and quality control of polyamides over the last 10-15 years, most of these sources of nonuniformity can be virtually eliminated.

New Interests In Old Procedures

Throughout the literature, one finds it emphasized that to obtain satisfactory level acid dyeings on wool or polyamides, it is necessary to dye at the boil 100C (212F). With the ever increasing cost of energy, however, people have found it now advantageous to examine acid dyeing at much lower temperatures.

Peters and Stevens (*8*) suggested in 1956 the use of organic solvents to assist in the dyeing of wool because these solvents accelerated dyeing at lower temperatures. They found that a premetallized dye, Irgalan Gray BL (Ciba-Geigy; C.I. Acid Black 58) exhausted completely on wool in 30 minutes at 60C (140F) in the presence of *n*-butyl alcohol.

The mechanism of this phenomenon was explained by Alexander and Stacey (*9*) by the assumption that the solvent breaks down the hydrogen bonds between dye molecules, thereby preventing the formation of dye aggregates in the dye liquor. It has also been suggested that the solvent is absorbed at the fiber/water interface and there it acts as a conductor for the dye molecules which are more soluble in the solvent than in water.

Beal, Dickinson and Bellhouse (*10*) did an extensive study of the effect of solvents in lower temperature dyeing in commercial applications. They concluded that benzyl alcohol was the most suitable compound to use for low temperature dyeing. Although it is expensive, it is practical to use because the exhaustion of the dyebath is so complete that the dye liquor can be used again without further purification.

Although this is a relatively old technique, its revival is predicted in the near future.

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Dyeing Primer: Part 3

Dyeing With Basic Dyes

By MATHIAS J. SCHULER, The Du Pont Co., Wilmington, Del.

BASIC dyes have been available and used for about 120 years. The dye mauve, synthesized by Perkin in 1856, is a basic dye. In addition to mauve, other synthetic basic dyes—such as fuchsine, methyl violet, aniline blue, etc.—were prepared and have been used for many years on such natural vegetable products as straw, raffia and jute.

Basic dyes have been used extensively for dyeing silk and cellulose acetate, but because of fastness deficiencies their use has gradually declined. Leather and paper, however, continue to be dyed with basic dyes.

In the mid-1950's the synthetic fiber material polyacrylonitrile became available. It was found that the positively charged colored ion of the basic dye, the cation, was attracted strongly by the negatively charged ions in the acrylic fiber and that the combination had unusually good light and wash fastness. Further, the brilliant shades characteristic of basic dyes on natural materials were retained. Since then many new dye structures have been synthesized so that there is an excellent selection available providing many options to the dyer.

ABSTRACT

Basic dyes are ionic dyes in which the colored part of the molecule is positively charged. They have good solubility in water, have high color value and are among the brightest dyes available.

The dyeing of acrylics by conventional retarder technology is used as a generalized example of dyeing with basic dyes.

KEY TERMS

Acrylic Fiber
Basic Dyes
Cationic Dyes
Dye Rate Compatibility
Fluorescence
Leveling
Retarder
Sites
Softener
Transfer

Distinguishing Characteristics

Basic dyes are ionic dyes in which the colored part of the molecule is positively charged (cationic). They have good solubility in water. As a class they have high color value and are among the brightest dyes available. An almost unlimited range of shades can be achieved having good fastness properties at reasonable prices. Many basic dyes fluoresce on dyed fabric.

Basic dyes are applied to fibers made up of negatively charged polymer molecules. Bonds can be formed between the cation of the dye and the anionic site in the fiber. At the end of the dye cycle the dye cations are almost completely absorbed or exhausted by the fiber. It is important that the number of dye cations does not exceed the available cationic groups in the fiber. If the amount of dye is excessive it will exhaust poorly, and in the case of blends this may result in substantial staining of the other fibers present.

Dyeable Fiber Types

Basic (cationic) dyes produce complete shade ranges on acrylic, modacrylic and modified nylon and polyester fibers. Since basic dyes for the most part are applied to the acrylics, this application will be used as the example here. A complete list of fiber names and deniers can be found in reference (*1*).

Preparation Of Fabric

For uniform application of basic dyes, it is absolutely necessary to prepare the substrate by removing surface additives required in knitting and weaving. The process is scouring, and for cationic-dyeable fibers, 1.0% nonionic surfactant, together with 1.0% tetrasodium pyrophosphate, can be used. Scour for 20 minutes at 140-160F. Follow with warm and cold rinses.

This procedure will be effective with conventional knitting and weaving aids, but some of the new materials on the market require special treatments. Therefore, whenever possible, fabric preparation should follow the manufacturer's recommendations.

Typical Dyeing Recipe

The following is a typical dyeing recipe for the atmospheric pressure dyeing of acrylics:

0.25%	EDTA sequestrant
10.0%	sodium sulfate, anhydrous
0.5%	nonionic surfactant
1.5-3.0%	retarder
0.5-1.0%	acetic acid (56%)
X%	dye mix (basic dyes)

Purpose Of Ingredients In The Recipe

- EDTA sequestrant: Ethylenediamine tetra-acetic acid is a chelating agent used to remove di- and trivalent metal cations from the bath as unionized soluble complexes, preventing off-shade dyeings due to metal ion effects with some dyes and precipitation of insoluble metal sulfates.
- Sodium sulfate anhydrous: Promotes transfer and leveling, functions as a mild retardant and stabilizes the shade of some dyes in the dyebath.
- Nonionic surfactant: Assists in wetting the fabric; is particularly useful in systems with basic dyes.
- Cationic retarder: Required to achieve level dyeings in a reasonable time in atmospheric pressure equipment. Retarders are actually colorless basic dyes that compete more or less successfully with the dyes for the negatively charged ionic groups. Thus fewer dye ions react with the ionic groups in the fiber in a given time permitting more uniform distribution of the dye. As exhaust proceeds some of the dye ions replace the retarder ions in the fiber.

This is the third in a series of 12 short papers on the fundamentals of dyeing. The series is intended for those who have had no formal introduction to the subject. Basically it will cover the application of various classes of dyes to various types of fibers. The series began in January and will appear monthly until it is concluded. (For a list of the topics to be covered, see page 25 of TCC for January.)

Larger amounts are required for the low concentrations of dye used in pastel shades. For heavy shades very little, if any, retarder is required.

- Softener: Helps to enhance the hand characteristic of acrylic fibers and assists in rewind operations. It is usually cationic so that it is retained by the fiber following processing.
- Acetic acid: Reduces pH to the range desirable for dyeing.

Dye Application Procedure

After scouring, the substrate is ready for dyeing according to the following procedure:

Set the dyebath at 120-140F with:

0.25%	EDTA sequestrant
0.5%	nonionic surfactant
10.0%	sodium sulfate-anhydrous
0.5%	acetic acid (56%)
1.5-3.0%	retarder

Run for 5 min then add X% basic dyes previously wetted with 1.0 to 1.5% glacial acetic acid in a small amount of hot water.

Adjust pH to 4.0-4.5 with acetic acid.

Raise temperature to 180F at 3F/min.

Raise temperature to 205-212F at 1F/min.

Run 1 to 1.5 hr as close to 212F as possible.

Cool to 170F to make dye adds and then raise to 212F. Hold for 20 min.

When the correct shade is achieved, cool slowly to 120F.

Rinse well.

Scour at 120-140F using 0.5% nonionic surfactant and 1 to 2% acetic acid (56%).

Rinse.

Apply softener according to manufacturer's directions.

Purpose Of Steps In The Procedure

The fabric/water/chemical combination is thoroughly mixed to uniformly distribute the components and to achieve complete wet-out. It is particularly important that the retarder has a chance to equilibrate with the fabric. The uniformity of retarder distribution is just as important to a level dyeing as is the uniform distribution of the dye.

Complete solution of the dye is important. Since basic dyes are most soluble in acid, either all or a part of the acid to be used in the dyeing can be added to the hot water used to dissolve the dye. Live steam should never be used to assist solution since tarring may result. If the older basic dyes are used, it is helpful to weigh them separately, wet them out with a small amount of concentrated acetic acid then add to hot water.

Dyeing proceeds best in an acid medium, and the dyes are more stable and soluble.

The temperature may be raised at 3F/min, a relatively fast rate, because little dyeing takes place on acrylics up to 180F. Agitation should be adequate to keep the bath and fabric uniformly mixed.

At about 180F many acrylic types approach the point of rapid dyeing, a point at which the physical structure of the polymer "opens up" to allow diffusion of dye into the fiber. Therefore, the rate of temperature increase is reduced so that the fabric "sees" a uniform concentration of dye and temperature.

One to 1.5 hours should be sufficient to achieve adequate dye penetration of the fiber at 212F. With the system at this temperature, there is practically no leveling with most basic dyes.

To make adds, the bath and fabric are cooled slowly to 170F. As above, little dyeing takes place at this temperature, giving the dye a chance to arrive at a uniform concentration throughout the bath. The temperature is raised to exhaust the dye add and permit penetration of the fiber.

After the required shade is achieved, reduce the temperature slowly to prevent crack marks in the fabric.

Rinse well to remove most of the dyebath additives.

Scour to complete removal of dyebath additives.

Rinse to remove surfactant.

Softener is used to enhance the hand or feel characteristic of the acrylics. It makes the result more wool-like.

Special Problems

Uniformity

Without question uniformity is the major problem associated with dyeing acrylics with basic dyes. Many suggestions for achieving uniformity or levelness have been reported in both the trade and the scientific literature. The problem is acute because at temperatures up to 212F, there is for all practical purposes no transfer or relocation of dye after its initial absorption (or "strike") by the fiber. If the initial dyeing is unlevel, the final dyeing will be unlevel. Unlevelness can be caused by temperature differences within the load as well as nonuniform circulation of the dyebath.

Temperature Differences

It has been reported that a 2F change in temperature results in a 15% change in rate of dyeing (*2*). Thus it is very clear that to achieve the most level dyeing, temperature differences in the load must be minimized in the temperature range above 180F where the dyeing rate is highest.

Poor Circulation

Concentration differences in the dyebath and liquor surrounding the substrate can occur as the result of poor circulation of the bath. If concentrations are different, the rates of dyeing will be different and nonuniformity of shade and strength will certainly occur. Every effort must be made to achieve uniform dyebath circulation throughout the run but particularly during the period of most rapid dyeing rate.

Compatibility Of Dyes

It is well known that the rate of dyeing of one basic dye can be affected by the presence of another in the bath. Under ideal conditions this is not a big problem, but where conditions are less than ideal the lack of dyeing rate compatibility can result in lack of shade uniformity of the dyeing.

A method for experimentally determining the rate compatibility of basic dyes combined in a dyebath was defined by Beckmann (*3*) and adopted as a test method by AATCC (*4*). The test method classified each basic dye into one of five Classes, 1 to 5. All dyes in Class 1 are compatible, as are those in Class 2 and so forth. This means that a dye formula made up of dyes selected from a single class will dye on shade from start to finish because each dye in the mix will dye the fiber at essentially the same rate.

Further, the rate of dyeing for dyes within a class is not concentration dependent. This means that in a three-dye formula, if all three dyes are from the same class, the dye shade will be essentially the same from start to finish even though the dye concentrations may be substantially different.

From a practical standpoint it is not always possible to select dyes for a formula that are from the same class. If the dyes are from classes differing by one, the results, while not as perfect, will be better than if no selection had been made.

Elevated Temperatures

While control of the variables discussed above is critical when dyeing at 208F, they are not as great a problem at a temperature of 235F. At 208-212F transfer of dye from one fiber to another is extremely slow. At 235F transfer is very significant, and splotchy dyeings can be considerably improved if not fully recovered.

Transferring Dyes

Basic dyes have recently become available that can transfer at 212F on acrylics. As more experience is gained in their use it is possible that the strict control suggested above may be relaxed.

Chlorine In The Water

When dyeing pastel shades in which very small quantities of dyes are used, it is often necessary to treat the water in the dyebath with an antichlor such as sodium bisulfite to destroy chlorine *before* adding the dyes. Many basic dyes can be destroyed by chlorine.

Understanding The Principles

The dyeing of acrylics and modified nylon and polyester fibers has been studied extensively, not only to improve application procedures but also to achieve better understanding of the fundamental principles involved. The following additional reading list is offered to assist the dyer in achieving a better understanding of both practice and theory.

- Asquith, R. S., H. S. Blair and N. Spence, *Journal of the Society of Dyers and Colourists*, Vol. 94, February 1978, pp49-52.
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(3) Beckmann, W. D., *Proceedings of the 11th Canadian Textile Seminar*, Canadian Association of Textile Colourists and Chemists, Montreal, August 1968, pp97-104.

(4) AATCC Test Method 141-1977, Compatibility of Basic Dyes for Acrylic Fibers, *AATCC Technical Manual*, American Association of Textile Chemists and Colorists, Research Triangle Park, N. C., Vol. 54, 1978, pp52-53.

Dyeing Primer: Part 4

Dyeing With Direct Dyes

By MARSHALL WHITE JR., American Color & Chemical Corp., Charlotte, N. C.

ABSTRACT

Direct dyes are a major class of synthetic dyes used in the coloring of cotton and other cellulosics—i.e., viscose rayon, linen, jute, hemp and ramie. They vary in light fastness from very poor to outstanding. Most have limited wet fastness in medium to full shades unless they are aftertreated.

KEY TERMS

Cellulosic Fibers
Direct Dyes
Dyeing

THE development of Congo Red in 1884 proved to be the forerunner of a large class of synthetic dyes for the dyeing of cellulosics. This class of dyes, known as the direct dyes, was named such because they dye cellulosic fibers directly without mordanting which was necessary when trying to dye cellulosics with virtually all naturally occurring dyes. The majority of the direct dyes are sulfonated azo compounds which ionize in an aqueous medium and the colored component or chromophore constitutes the anion.

Direct dyes represent an extensive range of products which are easy to apply and also are very economical. In 1977, the production of synthetic dyes in the United States was 264 million pounds of which 30.7 million pounds were direct dyes (*1*). While a large part of the production of direct dyes is consumed by the textile industry, approximately 25% goes for the coloration of paper, leather and other uses. Direct dyes are water soluble and can be applied to cotton and other cellulosic fibers such as viscose rayon, linen, jute, hemp and ramie.

Direct dyes vary in fastness to light from very poor (AATCC Class 1) to outstanding (AATCC Class 8) and are used for coloring materials requiring little or no fastness to light as well as those requiring maximum fastness such as automotive upholstery or draperies.

Directs also vary in fastness to washing, perspiration, pool water and other wet fastness properties, as well as staining effects on wool, silk, acetate, polyester, acrylic and other fibers. Most directs have limited wet fastness in medium to full shades unless they are aftertreated, but some are better than others.

Preparation of Substrates

All successful dyeing operations are based on the proper preparation of the materials prior to dyeing. Loose cotton, roving, sliver and yarn contain hardly any impurities except those which occur naturally in the cotton. Cotton knit goods may additionally contain a small amount of lubricant which was added to facilitate knitting. Woven goods of cotton will contain not only the natural impurities but also sizes which were applied to the cotton yarn to add strength for weaving. Starch sizes must be removed before scouring and dyeing by using a suitable enzyme. Materials which contain no size or which have been desized should then be scoured in a bath with a small amount of detergent and alkali such as soda ash or tetrasodium pyrophosphate for 20 to 30 minutes at 180-200F (82-93C), followed by thorough rinsing before dyeing. For light or bright shades, cotton is usually bleached with hypochlorites or peroxides.

Viscose rayon staple, yarn or knitted fabric can usually be entered directly into the dyebath without preliminary scouring. Woven fabrics of viscose rayon generally must be desized with a suitable enzyme followed by a scour with suitable detergent and mild alkali. Viscose rayon fabrics usually do not require bleaching prior to dyeing.

Typical Dyeing Recipe

A typical dyebath might contain: direct dye, water, sodium chloride or Glauber's salt (sodium sulfate decahydrate $Na_2SO_4 \cdot 10H_2O$) and an anionic wetting agent.

Water acts as the application medium. The dye dissolves in water, forming an ionized solution of particles ranging from monomolecular to large aggregates. It is thought that the dye anions in solution diffuse to the fiber surface and deposit on the fiber surface from which they diffuse into the amorphous areas of the fiber through pores. The dye anions are fixed in the fiber through hydrogen bonding and/or van der Waals forces. Addition of electrolyte in the form of sodium chloride or sodium sulfate is necessary for exhaustion of the dye since cellulosic fibers when placed in water take on a negative charge that would repel the direct dye anion. The addition of sodium chloride or sodium sulfate provides the sodium ion which in effect neutralizes the negative charge around the fiber and thus allows the direct dye anion to deposit on the surface of the fiber and diffuse into the fiber. Anionic wetting agents may be added to facilitate better wetout of the fiber.

Application of Direct Dyes

In dyeing properties, direct dyes fall into three main categories established by the Society of Dyers and Colourists (*2*):

- Class A. Dyes which level well even in the presence of considerable amounts of salt.
- Class B. Dyes with poor leveling

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properties but which can be dyed by regulating salt addition.

- Class C. Dyes of poor leveling properties which exhaust well in the absence of salt. The exhaust of these dyes is controlled by the rate of rise of temperature of the dyebath.

Less salt is required for Class C dyes for good exhaustion than for Class A and Class B dyes. Extreme care should be used in making salt additions with dyes in Class C, and caution should be exercised in making additions to salt controllable types in Class B. It is good practice to start with small additions of salt, possibly 2.5% on the weight of the fiber, and to double the amounts in subsequent additions until all the salt has been added. The total amount of salt will depend on the dye selected, the depth of shade and the liquor ratio, and will vary from 5-25% or more on the weight of the fiber. The dyes must be carefully selected, keeping in mind shade, fastness requirements, costs, rates of exhaust, leveling properties and salt sensitivity. Dyes with similar dyeing characteristics should be used together wherever practicable.

In the batch dyeing of direct dyes, the particular procedure employed will depend on the type of equipment (package, beck, jig, paddle and jet), the fiber form and the rates of exhaust of the dyes that have been chosen. Generally the fiber should be thoroughly wetout with a good wetting agent. The dye which has been previously dissolved by pasting with a little warm water, followed by diluting and boiling for about five minutes, is then added to the dye machine through a strainer or cloth. The dyebath is raised gradually to the boil, or to the highest practical temperature, and held for about 20-30 minutes. Salt is added and dyeing is continued while cooling to a predetermined temperature since most direct dyes have more affinity for cellulosics below 200F (93C). If the shade is satisfactory, the material is rinsed cold and usually aftertreated and then dried.

Direct dyes may be applied under pressure in jets, package machines and pressure becks provided dyes are selected which are stable to temperatures in excess of 225F (107C). When applied under pressure, as may be the case in dyeing disperse and directs on polyester and cotton blends, the dyebath is heated to 225-265F (107-130C) for exhaustion of the disperse dyes on polyester followed by cooling to 180-200F (82-93C) to effect exhaustion of the direct dyes.

Direct dyes may be applied continuously by padding through the dye solution and then fixing in a steamer. An improvement in fastness can be effected by using a boiling booster containing salt prior to steaming. Fixation is followed by rinsing and drying.

Aftertreatment of Direct Dyes

The fastness of selected direct dyes can be improved in several ways:

(1) Cationic active fixing agents improve wet fastness by combining with the anionic dyes to form more or less water insoluble complexes. Many cationic fixing agents are detrimental to light fastness.

(2) A number of direct dyes can be improved in wet fastness by aftertreatment with formaldehyde.

(3) The light fastness of some dyes is improved considerably by aftertreatment with a copper salt like copper sulfate.

(4) A cationic active agent and a copper salt are sometimes used in combination to improve both light and wet fastness. Usually a special preparation containing both components is supplied by the manufacturer.

(5) Some direct dyes can be improved in wet fastness by a simple aftertreatment with selected diazonium compounds such as diazotized paranitroaniline.

(6) Certain direct dyes which have a free amino group can be diazotized by treatment with sodium nitrite and sulfuric or hydrochloric acid and then developed with beta naphthol, metadiamino-toluene or other coupling agents. These dyes are known as developed or D & D (diazotized and developed) dyes. The size of the molecule is increased in the development, and wash fastness is much improved. The shade in most cases is entirely different after diazotization and development.

Suggested Further Reading

(1) Dominguez, G. S., "Direct Dyestuffs: Theoretical and Practical Aspects of Direct Dye Application," *Textile Forum,* October/November 1966, pp31-68.

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Dyeing Primer: Part 5

Dyeing With Vat Dyes

By CLAUDE S. HUGHEY, BASF Wyandotte Corp., Charlotte, N. C.

The use of vat dyes as coloring matter can be traced to ancient times when people used natural animal and plant derivatives to color their garments and other textiles. Some of the earliest references to such coloring substances go back thousands of years when Tyrian Purple was used. This dye was of animal origin, being an extract from shellfish.

Indigo was the most important of the natural coloring materials of the age. It was obtained from such tropical plants as Indigofera, and from the woad plant, Isatis Tinctoria, which was the earliest source of the color in Western Europe.

A tremendous new field of synthetic organic chemistry was formed with the discovery of a process by which vat dyes could be produced from coal tar. These dyes are typified by the presence of one or more keto or carbonyl groups. They are insoluble in water and have no affinity for textile fiber so long as they remain in an insoluble state.

ABSTRACT

Vat dyes are divided into two groups—anthraquinoid and indigonoid. The anthraquinoid type are noted for superior fastness properties, especially fastness to light. The indigonoid type offer brilliant shades that make them desirable for many uses.

KEY TERMS

Cotton
Dyeing
Dyeing Primer
Dyes
Exhaust Dyeing
Polyester
Thermosol Dyeing
Vat Dyes

Vat dyes are divided into two groups which are loosely called anthraquinoid and indigonoid. The anthraquinoid group exhibits superior fastness properties—distinguished by excellent fastness to light—and is the most widely used group.

A few of the indigonoid group of dyes are outstanding in brilliance of shade. This characteristic combined with fastness to washing and bleaching of some of the dyes makes them desirable for many uses. They are also used in some applications simply for economic reasons. Vat dyes are used to dye cellulosic fibers in relatively dull shades requiring good fastness to washing, particularly when fastness to chlorine is essential. This class of dyes encompasses a group of complex organic chemical products that can be applied by continuous or exhaust procedures. The nature of the dyes and their sensitivity to variations from established techniques of application require close adherence to proven procedures. Shade reproducibility is excellent when adequate regard is given to procedures.

Uses

Vat dyes are particularly suited for use on cotton and rayon substrates. They are also used to dye nylon and to stain polyester in blends with cellulosic fibers because of the dyeing effect on these fibers under proper conditions.

Fabric Preparation

Substrates to be dyed with vat dyes are generally bleached, and in many cases mercerized. Mercerization enables the dyer to build deeper shades and to dye the dead or immature cotton. Many dark brown and navy shades, however, can be dyed on an unbleached substrate that has only been desized and mercerized.

Typical Dyeing Recipes

Continuous Dyeing

All-Cotton Fabrics: (a) Dye Pad: Vat dye, migration control chemicals, wetting agent. (b) Chemical Pad: Caustic soda ($NaOH$), sodium hydrosulfite ($Na_2S_2O_4$), sequestering agent, dispersing agent. (c) Oxidize and Soap: Hydrogen peroxide or sodium perborate, acetic acid, detergent (anionic surfactant).

Polyester/Cotton Fabrics: (a) Dye Pad: Disperse dye, vat dye, migration control chemicals, pH control agent, wetting agent. (b) Thermosol unit is necessary to fix disperse dyes in the polyester. (c) Same as (b) and (c) above for all-cotton fabrics.

Exhaust Procedures

Vat dye, caustic soda, sodium hydrosulfite, leveling agent, sequestering agent.

(For a full discussion of processes and recipes, see reference 4 under Suggested Reading.)

Role Of Chemicals

The purpose of the various chemicals used in vat dyeing procedures is as follows:

Continuous Dyeing

(1) Migration inhibitors are necessary to control dye particle movement during the predrying phase.

(2) Wetting agents are generally used (but not always required) to insure uniform and rapid wet-out of the fabric. They also help to promote an even uptake of dye in the fabric throughout the lot being dyed.

(3) Caustic soda and sodium hydrosulfite are necessary to reduce the insoluble dye particles to the soluble leuco form.

(4) Hydrogen peroxide or sodium perborate is used to oxidize the dye back to the insoluble form.

(5) Acetic acid is used for pH adjustment.

(6) Sequestering agents are used to chelate metallic ions which might interfere with dye fixations.

This is one of a series of short papers on the fundamentals of dyeing. Intended for those who have had no formal introduction to textile dyeing, the series basically will cover the application of various classes of dyes to different types of fibers.