DYEING

1. Introduction

For those that see color, the world is a colorful place. Most humans have color vision and enjoy and appreciate the wide palette of Nature. We use colors to imitate Nature, and to decorate our environment, our food and ourselves. For most color under human control, a colorant can be included as the item is formed (such as for an extruded plastic object) or combined in some medium that is applied to a surface (eg, paints, cosmetics). For clothing, furnishing, and much besides, textile materials are ubiquitous. There is a need for the ability to control or change their color: The process of dyeing is used to color them. The same dyeing process is occasionally used to color paper and leather, and textiles can be colored by non-dyeing means, but textiles and dyeing have a high degree of mutual inclusivity.

The global consumption of textiles as the twenty-first century began was estimated at $\sim$50 million tons per year, with polyester and cotton accounting for $\sim$75% of the total. Fiber use has generally increased at a rate faster than the growth of population. Dye is applied to these fibers at an average rate of 1–2%, ie, annual production of synthetic dyes is $\sim$750,000 tons (1,2).

Dyeing occurs when a soluble colorant is adsorbed at the surface of a fibrous substrate, and then diffuses into the substrate. What follows is a detailed examination of that basic process in both theoretical and practical terms.

Colorants are typically divided into dyes and pigments. The demarcation between them is based chiefly on solubility: A pigment relies on insolubility in the medium in which it is dispersed, while a dye requires some degree of solubility, maybe low, maybe temporary, that will allow it to diffuse into the polymeric matrix of a textile fiber. In order for a colored substance to be regarded as a useful dyestuff, factors beyond solubility are required. A dyestuff must be substantive for a textile and thus be preferentially taken up by the fiber, usually from an aqueous solution. The uptake should be high enough to be economic, and the rate at which the dyeing occurs should be controllable to give a uniform, level result. The dyed textile should have satisfactory fastness for the intended end use. The process of dyeing therefore combines chemistry, application technology, economics, and customer needs.

Dyeing is an ancient practice. Originally all dyes were of natural origin obtained locally from plants and even animals. The first synthetic dyestuff, mauveine, was invented by Perkin in 1856 in the United Kingdom in a naÿve attempt to synthesize quinine from coal tar derived intermediates. The story has been the subject of a popular book (3). His discovery led to many other derivatives of coal tar as coloring matters, and, ultimately, to industrial organic chemistry. The first diazonium salt derived from picramic acid was prepared in 1858 and diazotization of aromatic amines with subsequent coupling is still the basic chemistry behind the majority of commercial colorants. The technically important natural dyes alizarine (from madder) and indigo were synthesized and commercialized in the 1870s and 1890s, respectively, and soon supplanted the natural versions. Over the first two decades of the twentieth century, synthetic dyes came to dominate the market and have continued to do so.

The desire for things natural is ever present, with cycles of popularity that bring the subject occasionally to the forefront. With the increased awareness of environmental and “green” issues at the end of the twentieth century there was a corresponding interest in natural dyes together with a preference for natural fibers over synthetic. Many factors conspire to confine the use of natural dyes to a very small proportion of the world’s textiles. The products are subject to seasonal variations of quality, and consistency of color is a problem for the dyer, although some efforts are being made to commercialize the extraction of consistent material. The range of colors achievable is more limited than with synthetic dyes. Moreover, studies have shown (4) that if current production of cotton were colored with natural dyes, at least 31% of the available world’s agricultural land would be needed to cultivate the requisite plants, and require the disposal of 170 million tons of spent plant waste. The estimate is based on it taking roughly 450 g of fresh dye plant to achieve the same tinctorial effect as 1 g of synthetic dye. Work to increase the dye content of plants via genetic modification has been explored, although given the debate about genetically modified (GM) crops it becomes an interesting question whether dyes thus derived are still “natural”. The application of natural dyes, especially on cotton, usually requires the use of metal mordants: while iron and aluminum are relatively benign, chrome, tin, and copper should be strictly controlled. Estimates of the cost of dyeing cotton with natural dyes suggest that it is one or two orders of magnitude greater than dyeing with synthetic dyes. In short, the use of natural vegetable dyes to color anything but a tiny proportion of the world’s textiles is both environmentally and logistically impossible (1,5)

As fairly complex organic chemicals, some logical generic cataloging of dyes (and pigments) is useful, and this is provided by the *Colour Index* (CI) published jointly by the Society of Dyers and Colourists in the United Kingdom and the American Association of Textile Chemists and Colorists. First published in 1928, it is now in its 4th edition. While previous editions have been in hard copy (6) the latest version is available only via web-based subscription (7).

Some details vary from edition to edition, but generally dyes are listed both by chemical type (where the chemical structure is known) and, most usefully from the dyer's point of view, by application characteristics. In this article, classification by application method is chiefly used. The two listings are cross-referenced, and supplemented by a list of commercial names under which each dye is sold. The CI also includes information about fastness properties, application details, and usefulness on nontextile substrates. For a discussion of the classification of dyes, see the article DYES AND DYE INTERMEDIATES.

The *Colour Index* assigns CI generic names to commercial dyes. A CI Generic name takes the following form: C.I. [Dye application type] [Color] [Number], e.g. C.I. Acid Red 102. The main CI dye application types are acid, mordant, direct, reactive, sulfur, vat, azoic, disperse, and basic: these are discussed in more detail in later sections where their application to particular fibers is discussed. The colors are restricted to yellow, orange, red, violet, blue, green, brown, black and (for pigments) white. Numbers are assigned sequentially.

A given generic name is shared by dyes of the same nominal chemical constitution. Dyes and pigments are marketed as preparations which include diluents, dispersants, or other chemicals. Colorants other than the essential colorant may be present as a result of impurities in starting materials or as an inevitable result of the reaction conditions used: it is rarely economic or even beneficial to purify dyes. Minor additions of "shading components" may also be used to provide a consistent product. The Colour Index implies only that their essential colorants have the same chemical constitution. Differences in a dyeing process can derive from the physical form of the colorant, for example, its dispersion quality. It has been demonstrated that products with the same CI generic name do behave differently and that preparations vary in purity or consistency of strength (8). It should not be assumed that one commercial brand can replace another in every respect.

While there is obviously a need for a generic classification, most especially in the accurate description of dyes being traded internationally, and in their toxicological profile, the factors described above have led to some considerable controversy about the continued use of the CI system for the generic classification of dyes, and several major manufacturers no longer list or supply their products under this classification. Whatever the future of the Colour Index, its classification method is firmly established and used to differentiate dyes for different fibers.

2. The Dyeing Process

2.1. Fibers.

For dyeing to take place, the polymeric substrate must be accessible to dye molecules. The range of natural and manufactured (both regenerated and synthetic) fibers means that access can be considered differently in different cases.

Fiber Types and Variations. Fibers may be natural or manufactured, hydrophilic or hydrophobic, nonionic or ionic. Natural fibers vary with (sub-)species of plant or animal and with growing conditions experienced as the fiber forms. Grading, sorting and blending are carried out to provide a reasonably consistent product. Synthetic fibers are generally more consistent, but are available in a myriad of variations (often distinguished by “type numbers”). A given manufactured fiber can be supplied with different finenesses (deniers), cross-sections, and most are delustered to some degree by the inclusion of titanium dioxide in the melt or solution from which the fiber is extruded. Most manufactured fibers are drawn after extrusion to obtain better mechanical properties by the development of increased orientation and crystallinity of the polymer chains. Manufacturing variations of the resulting polymer morphology leads to subtle variations in the rate or extent of dye uptake, to the frustration of a dyer trying to achieve a level dyeing. Manufacturers provide merge numbers: fabrics consisting of fibers of one merge should dye level, but a fabric of “mixed merges” will tend to dye unlevel.

The general chemical rule of thumb that “like dissolves like” corresponds in dyeing to “like dyes like”: Hydrophilic substrates are dyed with hydrophilic dyes and hydrophobic dyes dye hydrophobic fibers. Nylon, acrylic and modified polyester fibers have ionic groups in the polymer, or at the end of polymer chains, and while the polymer has overall hydrophobic character, these fibers are capable of being dyed by water-soluble dyes of the opposite charge.

Hydrophilic Fibers. Cellulose and protein substrates (cotton, rayon, lyocell, linen, silk and wool, etc) are hydrophilic, and absorb water readily. The absorption of water by wool is less immediate because of hydrophobic surface scales, but in a dyebath the fiber is swollen with water. The model for the uptake of dyes by these fibers is thus one of water-filled pores through which soluble dye diffuses. The distinction is often made between the internal (fiber) phase and external (dyebath phase). The external phase consists of the mobile molecules that are in the external dyebath so far away from the fiber that they are not influenced by it. The internal phase comprises the water that is within the fiber infrastructure in a bound or static state and is an integral part of the internal structure. Dye molecules have different chemical potentials when in the internal solvent phase than when in the external phase. Also, in the external phase acids or bases are completely dissociated and give an external or dyebath pH. In the internal phase these ions can interact with the fiber polymer chain and cause ionization of functional groups. This results in the pH of the internal phase being different from the external phase and the theoretical concept of internal pH (9). The detailed physical chemistry of the dyeing process for hydrophilic fibers relies in part on assumed values for the internal volume of a fiber, and internal pH is particularly useful when the interaction of cellulose with reactive dyes is considered.

Hydrophobic Fibers. Hydrophobic fibers absorb comparatively little water, and “internal solution” has little meaning. These fibers are typically thermoplastic, and undergo a glassy–rubbery transition at a characteristic temperature, the so-called glass-transition temperature T_g. Above this temperature the polymer chain segments are mobile, and at any given time there is a free volume within the polymer matrix. The fiber is thus better regarded as a system of continuously changing regions of “free volume” through which dye can diffuse. The value of T_g in a polymer can be determined experimentally, and these values can give useful comparative information. The measurement is not carried out in an aqueous environment, however, and it is occasionally more realistic to consider a "dyeing transition temperature" that is defined by a temperature at which there is a rapid increase in the rate of dye diffusion through a polymer under aqueous dyebath conditions.

A more thorough discussion and comparison of the pore and free volume models is available (10).

Zeta Potential. When a textile is immersed in water and relative motion exists between the two a negative charge is developed on its surface. This is called the electrokinetic or zeta potential (11). This happens even with ionic fibers in neutral dyebaths, and values in dilute electrolyte ranging from -17 to -44 mV have been measured. Negatively charged dyes therefore are coulombically repelled, and uptake is reduced unless electrolytes are present to diffuse this charge. Similarly, cationic dyes are ionically attracted, and initial uptake (strike) may be rapid and unlevel unless precautions are taken. Since dyeing is a penetration of dye within the fiber structure, this surface charge is not useful in providing an attractive force between dyes and fibers. The zeta potential of a fiber is, however, useful for "exhausting" cationic materials onto the surface of a fiber. Thus cationically charged pigment and/or binder materials can be attracted to a fiber surface, and fixed in a subsequent curing process. This is the basis of the oxymoronically titled process of "pigment dyeing". The attraction of a cationic material to this fiber surface charge is also commonly used in household laundry when a fabric softener is applied in a rinse cycle: similar softening can be carried out in the rinsing steps after a commercial dyeing process.

2.2. Water: The Medium for Dyeing. Water is a polar solvent that interacts with both dyes and fibers. Dyes are often ionic, and the colored ion is solvated by water. Nonionic dyes typically have polar groups that interact with water, and provide limited but essential solubility. Other parts of a dye molecule may be hydrophobic, and have positive or negative effects on the local water structure. Water is sorbed by fibers and in many cases creates a swollen substrate through which dye can diffuse. Overall, the transition from a dye dissolved in water to one bound to a substrate is accompanied by changes in the binding of water with both components, with concomitant effects on the energy changes that drive the process (12,13).

From the practical point of view, in the course of preparation before dyeing, dyeing itself, and rinsing processes after dyeing, ~100 L of water are used per kilogram of material processed. This figure is typical, but may vary up or down by up to one order of magnitude depending on the details of the substrate and the processes used. Such large volumes of water may be obtained from a variety of sources: local rivers, municipal sources, private wells, and so on. Ideally, dyeing would take place from a pure medium, but in practice, it is uneconomic to purify large volumes of water when experience has shown that certain levels of impurity can be tolerated.

There is no one specification for satisfactory dyehouse water: The wide range of dyes, substrates and processes allow for different water purity requirements. Generally of concern, however, are alkalinity, hardness, and heavy metals. A rough guide to a satisfactory range of impurities for a dyehouse trying to make best use of instrumental match prediction has been suggested (14). The chief of these are detailed in Table 1.

Table 1. **Suggested Specification: Dyehouse Water for Instrumental Match Prediction in Yarn Dyeing**

Item	Specification ppm
hardness ($CaCO_3$)	10–25
alkalinity ($CaCO_3$)	35–65
iron	0.02–0.1
manganese	0.03
dissolved solids	65–150
suspended solids	0

Since many processes associated with dyeing are pH controlled, the pH (or, more strictly, the alkalinity, since this will govern the amount of adjusting material required) of incoming water should be monitored and adjusted if necessary. Many dyeing processes control pH, either as a positive controlling mechanism, or to avoid negative effects (such as dye instability). Hardness can reduce the solubility of dyes and form soap scums. Heavy metals, most often iron, manganese and copper, are common impurities. These can interact with dyes that have chelating groups and significantly change the shade of a dyeing. Not only must the dyebath be treated, but so must the rinse waters. Iron and copper can also catalyze the decomposition of peroxide, or accelerate the free radical attack of cellulose in a bleaching process. The addition of a sequestrant or chelating agent [both inorganic phosphates, or organic materials such as ethylenediaminetetraacetic acid (EDTA)] to water is common practice when these impurities are likely.

Hardness, heavy metals and to some extent pH can be dealt with by the use of ion exchange resins. Where these impurities are constantly present and interfere with operations, plant water can be routinely treated and supplied to the sensitive parts of the overall wet processing scheme.

Water from municipal sources is often treated with low levels of chlorine as a final sanitizing step. Even low levels of chlorine can effect the shade of some dyes, and a prudent dyer would add an antichlor (such as sodium metabisulfite) to a dyebath if chlorine is present.

Solvent Dyeing. The use of media for dyeing other than water has been examined. In the energy-conscious early 1970s, the lower amounts of energy required to heat organic solvents to dyeing temperatures, was expected to make solvent dyeing technically important and the technology was discussed and researched extensively (15,16). This interest did not materialize into practical acceptance, chiefly on cost and environmental grounds, and the techniques have not achieved importance.

2.3. Attractive Forces between Dyes and Fibers. Assuming that the fiber is accessible, what are the bonds formed between dyes and fibers that lead to the concentration of dye within the fiber and its depletion from solution? Together with the dye–water and fiber–water interactions, these forces lead to the overall attraction between dye and fiber, its affinity or substantivity, that is considered in more depth later. The forces of attraction between a dye and fiber are those that apply in any (organic) chemical system. The subject as it relates to dyes and fibers has been examined extensively (the whole of Refs. 9,10). While covalent bonds do ultimately contribute to the linking of reactive dyes and fibers, these occur only after other (secondary) forces have brought dye and fiber together. For most dye–fiber systems, only non-covalent bonding operates.

At one end of the scale are the coulombic or ionic forces that operate between anions and cations. There is a strong attraction between dye and fiber when oppositely charged. Water-soluble dyes and hydrophilic fibers contain salt groups that may dissociate to varying degrees in water. The charges may be dependent on pH. In the dyebath, fibers may be anionic or cationic, with an appropriate counterion. Likewise, the dyestuff can consist of a colored ion and a counterion. In some cases, depending on pH, the dye and fiber might carry similar charges. The resulting repulsion is counteracted by the other forces and the repulsion is used as a means of controlling the rate of uptake of dye. Ionic forces are obviously the simplest to contemplate, but a recognition that the ions of simple electrolytes do not exhaust as do dyes demonstrates that ionic forces are never the complete story.

Ionic dyes or fibers also interact with dipoles (bonds with electrons that are unequally shared and which thus have slight negative and positive character). Dipoles interact with each other: a special case of dipole–diole interaction is the hydrogen bond. Dipoles can also induce dipoles in nonpolar bonds: the induced dipoles also contribute to the interaction of these partially charged species. Any discussion of the role of dipoles in dye-fiber bonding is complicated by the presence of water: chiefly as the medium for dyeing, but even as adsorbed water from the atmosphere. Water is highly (di)polar, and if dipoles of dye and fiber are to interact with each other, or with ions, or to induce dipoles in nonpolar bonds, one must assume that water can do likewise.

In other words, for the dye-fiber bonding to take place, such bonding has to replace the bonding of both dye and fiber with water: In the case of the dye, the interaction with water represents its solubility. For dyeing to take place to an economical extent (ie, in which the great majority of the dye is ultimately bound to the fiber) the *net* energy (enthalpy and entropy) change must drive the process forward, and any positive contribution from the formation of dye-fiber bonding must outweigh any negative contribution from the loss of bonding with water. Different sources categorize the forces based on dipoles in a number of different ways: most simply they can be categorized together as polar van der Waal's forces.

The relative importance of the different categories of dipole-based force has been the subject of much study and argument. There is more general agreement about the forces that derive from the transient dipoles of non-polar moieties. Dyes and fibers have aromatic and aliphatic hydrocarbon groups that are involved in such bonding, referred to variously as non-polar Van der Waal's forces, London forces, or dispersion forces. They are strong at close range, and can overcome the coulombic repulsion between similarly charged dyes and fibers: if the dye and fiber molecules can be brought close together, then these stronger dispersion forces dominate. This appears to be a key phenomenon in dyeing cellulosic fibers. The apparantly greater contribution of these forces in relatively large molecules is the basis of most of the rules of thumb involving “size and shape” comparisons of dyes.

The tendency of hydrophobic groups, especially alkyl chains present in synthetic fibers and disperse dyes, to associate together and escape from the aqueous environment is occasionally referred to as “hydrophobic bonding”. Dispersion forces are a major contributor to such bonding.

Aggregation of Dye. The above forces are considered simply as those that apply between dyes and fibers. Of course, intermolecular forces are at work between polymer chains of the fiber, and these contribute to the accessibility of fiber to dye. Additionally, dye–dye interactions also occur, and these have considerable practical importance. While simple ionic dye molecules dissolve readily, larger and more complex dye molecules tend to aggregate in solution as ionic repulsion of groups in one part of the molecule are counterbalanced by the attractive intermolecular forces that occur between other parts. Dyes can thus mimic surfactants in combining hydrophilic and hydrophobic properties in the same molecule, and dye aggregation shares some characteristics of micelle formation in surfactants, although experimental measurement of the degree of aggregation has proved difficult. Practical problems arise when aggregates break down over a limited temperature range, leading to a rapid availability of dye for uptake by the fiber and possibly unlevel absorption. Ultimately, in nonionic dyes, such as disperse dyes and unreduced vat dyes, the dye is only sparingly soluble, and exists in the dyebath as a dispersion of fine particles, even at elevated temperatures.

Additional Contributors to Fastness. The sum of the above forces provides the attraction between dye and fiber to drive the dyeing process forward. They also combine to keep the dye associated with the fiber in subsequent use, ie, they give the dye resistance to removal, or fastness, to agencies such as laundering or other wet treatments that might remove it from the fiber. In many cases, however, there are additional contributors to fastness that occur subsequent to the operation of these forces.

Once the dye is sorbed into the fiber (or even concurrent with its sorption) a dye may undergo a chemical reaction with functional groups within the fiber to form covalent bonds. This is the characteristic of reactive dyes (see DYES, REACTIVE). The covalent bonding of the dye and fiber subsequent to sorption provide the dyeing with good wet fastness properties.

By definition, dyes are soluble entities during the dyeing process. However, dyes may, after sorption into the fiber, undergo a chemical change to become insoluble, or revert to insolubility. This is the case with azoic/ingrain dyes, and vat or sulfur dyes, respectively. Since they are thus less hydrophilic, they are less prone to later removal by aqueous agencies.

2.4. Batch Processes for Dyeing.

For the most part, dyeing is accomplished in batch processes. While the practical details might make the process appear very different, the basic batch dyeing process can be summarized thus (Fig. 1).

A textile substrate is immersed in a bath of (usually) water in which dye is dispersed or dissolved. With agitation and heat, the dyestuff diffuses through the solution (**b**), is sorbed at the fiber surface (**c**), and then diffuses into the fiber (**d**). If the dye is aggregated or dispersed, the sequence is preceded by a dissolution of dye or breakdown of aggregates (**a**). Studies of the dyeing process that seek to explain dye-fiber interactions are usually based on this basic batch dyeing process. The physical chemistry associated with dyeing has been described and discussed in some detail over many years (17–21). This large volume of research work and published papers has put dyeing phenomena on a sound theoretical

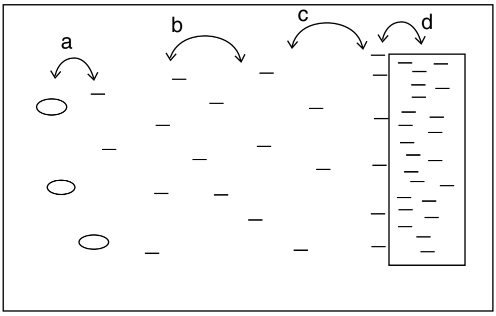

Fig. 1. Schematic dyeing process.

basis. The two major areas studied are a) the mode and strength of the interaction between dyes and fibers, the thermodynamics of the dyeing process, and b) the rate at which dyeing takes place, i.e. the kinetics of the process. While these studies have satisfactorily explained the machanisms of dyeing, the detailed results do not always correspond to real life dyeings, and theory relies on a number of assumptions.

Both practically and theoretically, some basic concepts and terms are commonly employed.

Liquor Ratio. The aqueous medium in which dyeing takes place is called the “dyebath”. The liquid with the dissolved dye and auxiliary chemicals is traditionally referred to as the “dye liquor”. The ratio of the mass of the bath to the mass of the substrate (be it fiber, yarn or fabric, etc) is thus referred to as the “liquor to goods ratio”, or, more simply, “liquor ratio”. Higher (or longer) liquor ratios provide more level dyeings, but are less efficient in the use of energy, water and chemicals. The liquor ratio may be a function of the machinery used.

%owf. The amount of dyestuff applied to the substrate is measured in percentage terms as “percent on weight of fiber” or “%owf”. Occasionally “mass” is substituted for weight, and “goods” for fiber, hence “%owg” or “%omf” are essentially equivalent. The use of a percentage relationship means that a recipe is readily capable of translation from the laboratory to the bulk scale.

Strike. The initial sorption of dye by the substrate surface can happen in a short space of time. This is referred to as the “strike” of the dye.

Exhaustion. As dyeing proceeds, and dye moves from the bath to the fiber, the dyebath becomes exhausted of dye. The process of depleting the bath, and thus dyeing the fiber, is referred to as exhaustion, and dyes are said to exhaust onto the fiber. A high (degree of) exhaustion is obviously efficient in use of dye, but may limit the degree to which leveling or migration can take place. Exhaustion is usually referred to in terms of a percentage of dye that has moved from the bath to the substrate. Exhaustion over time may be illustrated by an exhaustion diagram (Fig. 2). Dye is initially sorbed rapidly, but the rate of uptake decreases as the dyebath is depleted of dye. Eventually, no further uptake occurs.

Levelness. This refers to the even distribution of dye throughout the substrate. An uneven distribution at the microscopic level is normal and tolerable, since the visual impression is still one of an even coloration. Larger scale

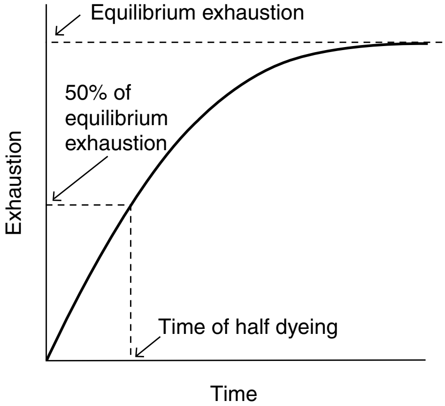

Fig. 2. Exhaustion–time plot of a dyeing process.

unlevelness that is apparent to visual inspection is a fault in dyeing. Levelness is achieved either by a level initial strike of dye or by the migration of dye as dyeing proceeds in a process of leveling. Leveling thus leads to levelness. Some dyes level readily, while others level only slowly: in the latter case even initial uptake is vital. Figure 3 represents the situation when a dyed textile is placed in a blank dyebath with an undyed piece of material. Material dyed with a dye that levels well (A) will lose dye and the undyed piece will pick it up (A′): eventually, the two pieces will be the same color: at the same time, a considerable amount of dye is present in the bath (A″). A material dyed with a dye that levels poorly (B) will lose little dye to the bath (B″) and thus, in a reasonable time, little is transferred to the undyed piece (B′).

Equilibrium. Dyeing is largely a physical process in which a dye equilibrates between the dyebath and the substrate. While most dyeings reach a point at which the concentration of dye in the dyebath is changing very little

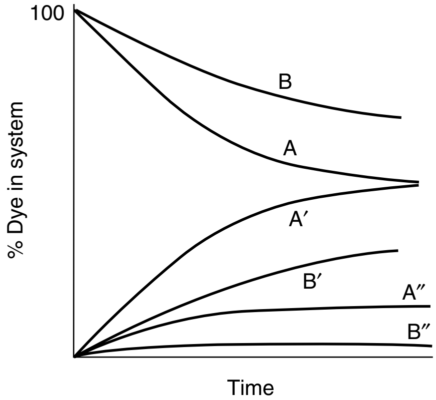

Fig. 3. Leveling behavior of dyes: A represents a dye that levels well, B a dye that levels poorly.

(see Fig. 2) it is doubtful whether many real dyeing processes reach true equilibrium, in which all fibers are uniformly and fully penetrated by dye, and dyebath concentration is constant. Nonetheless, equilibrium is an important concept when examining the theoretical aspects of the dyeing process. Like other chemical equilibria, dyeing reaches a dynamic equilibrium: the net concentrations of dye in fiber and in solution do not change; nonetheless, dye is still migrating from bath to fiber and vice versa. This is the basis of the migration that is important in obtaining a level dyeing.

2.5. Continuous Processes for Dyeing.

When large amounts of a single color (shade) are required, continuous processing is more efficient. Uncolored material is fed into the system, and colored material withdrawn, continuously.

Padding. The substrate is impregnated initially with dye solution, typically by dipping and a squeezing between rollers to remove excess and leave a consistent amount of dye on the substrate. This dip and squeeze sequence is referred to as padding. All the chemicals required for dyeing may be present in the pad bath; alternatively, some may be applied in a second padding step, usually after an intermediate drying.

Fixation. The penetration of fiber by dye akin to that which happens in a batch dyeing occurs in a fixation step. This might be accomplished with steam, dry heat, or simply a time delay while the fabric is stored on a roll.

2.6. Printing.

When textile substrates are printed with colored designs, dyes or pigments can be used. Currently, the market is approximately evenly divided between the two. Most printing is a continuous process. When dyes are used, the dye is applied to the fiber in a paste thickened to control its rheology and thus its transfer onto the fabric and the sharpness of the printed design obtained. The paste may also contain the chemicals required for fixation.

3. General Dyeing Practice

3.1. Dyers' Controls.

Agitation. A practical dyeing process requires stirring to achieve initial level sorption and for subsequent migration, and to make diffusion through the fiber the rate-determining step. In practice, the dyebath or the substrate can be moved, sometimes both. Depending on the particular machine the process may need to be adjusted: A machine that agitates more gently may need a procedure designed to cause a slower initial strike of dye. Machines are designed to generate turbulent flow.

Liquor Ratio. The liquor ratio may be dependent on the machine and the amount of substrate to be dyed, and so not fully under the dyer's control. As the liquor ratio increases the dyebath is more dilute and dye has a longer and slower diffusion path through it. A level initial strike is easier, and later there will be more dye in the bath for migration and leveling. However, a higher liquor ratio means that less dye will exhaust, more auxiliaries are needed to when these are applied in terms of their concentration in the bath, there is more water use, and thus more energy use. Naturally enough, for efficiency, the trend is to lower liquor ratios. Batch dyeings can be done in liquor ratios of 5:1 or less, but need a machine with good agitation. In continuous, pad batch, and printing processes

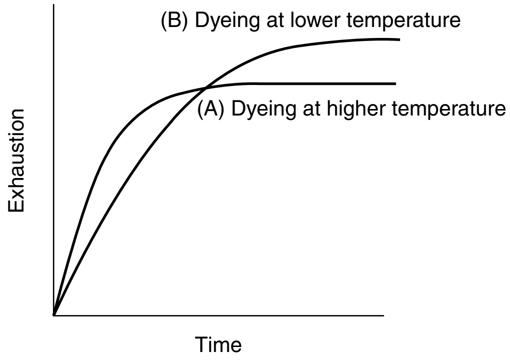

Fig. 4. Effect of temperature on dyeing rate and equilibrium exhaustion.

of dye application the effective liquor ratio may be less than 1:1, which accounts for the generally greater efficiency of those processes.

Temperature. Since dyeing is an exothermic process, an increase in temperature will displace equilibrium in favor of the dyebath. In other words, equilibrium exhaustion is lower at higher temperatures (Fig. 4). The effect is always present, but the size of the effect varies. The additional dye left in the bath at higher dyeing temperatures obviously is less efficient, but together with the greater energy in the system it means better leveling. More importantly, a higher temperature of dyeing increases the rate of dyeing, and the rate at which equilibrium is attained. In a practical dyeing time, some slow dyeing dyes may not approach equilibrium at a lower temperature, and consequently greater exhaustion is obtained (in a given time) at a higher temperature. Dyes that exhaust quickly may reach equilibrium in a practical dyeing time, and for these dyes, a lower temperature gives better exhaustion. Thus dyes may be described in terms of a “temperature of maximum affinity” despite the universal truth of a lower equilibrium exhaustion with increased temperature. In practice, a dyeing is usually begun at a low temperature and increased at a rate that provides even strike. The bulk of the process is carried out at a temperature that allows quick and level dyeing, for a time that gives sufficient penetration of the fibers. When exhaustion is significantly higher at lower temperatures (ie, a large gap between curves A and B in Fig. 4 at extended times) some additional exhaustion is obtained by cooling the bath while dyeing continues at the end of the process.

Auxiliaries. Auxiliaries are the chemical additions to the bath to aid the dyeing process. They may be added before or during the process. They may interact with the fiber, or with the dye. They may increase or decrease rate of dyeing, increase or decrease extent of dyeing. They include salts, pH modifiers (acids, alkalis), leveling agents, migrating agents, carriers, solvents, fixing agents.

3.2. The Aims of a Dyer.

The aims of a dyeing can be summarized as follows:

The Correct Shade. Much of this discussion is based on the science of color and color measurement that is beyond the scope of this entry. The reader is referred to the extensive literature on the subject (22–24).

A dyer is usually trying to match the color of some “standard”, and should know under which light source the match is to be judged. The standard was typically supplied by the customer in the form of a colored object: a piece of fabric, a piece of paper, a piece of yarn, etc. Sometimes these real physical samples are obtained from a standardized commercial set (Munsell, Pantone, SCOTDIC, Colorcurve, etc). All real physical samples have the disadvantage of changing with age and handling. While dyers have become familiar with instrumental color measurement, designers and specifiers have been slower to adopt numerical/ electronic color specifications, but as the textile supply chain has become global, the move to numerically based standards has accelerated. It is helpful if the standard is as color-constant as possible under different lighting conditions (25).

Achieving a specific color typically involves a mixture of three dyes. While the ideal primaries are yellow, magenta and cyan (that together with black make up the “process colors” used in color printing on paper and packaging) the usual dyeing primaries are yellow red and blue, since the phthalocyanine chromogens that provide most cyan colors do not have good dyeing properties. The mixture used should be formed of dyes that have compatible dyeing behavior. If the hue of the fabric is the same throughout all stages of dyeing, simply becoming stronger with time, and the hue of the final textile is reproducibly uniform both on its surface and within its interior. Compatibility is mainly a function of exhaustion rate, but can also be influenced by migration. If dyes in combination are compatible then the overall dyeing process can be shorter, reproducibility improved, and the chances of obtaining level dyeings improved (26).

In order to develop a recipe (a mixture of dyes) that will provide a match to the standard, dyers would typically use a trial and error process on the laboratory scale. The initial choice of dyes would be based on experience. It was common to “tweak” a previous dyeing of a similar color. Ideally, the match should be good under all light sources but this is not true for matches that are “metameric” (ie, that match in one light source but not in another). Metamerism can be reduced by the choice of dyes used to create the color, but never completely eliminated if different colorants are used to make the match than are present in the original standard.

In addition to the quantities of dye required, a commercial dyeing recipe includes all the other variables that are under the dyer’s control. These include the additives to the dyeing (auxiliary chemicals such as electrolyte, pH adjustment, leveling agents, etc), the time/temperature profile and the liquor ratio. Some of these may be dictated by the machinery available, for example, the liquor ratio and the degree of agitation (which in turn might control the rate at which the temperature can be increased). It is sometimes thought surprising that dyeings are rarely completely reproducible, but a consideration of the variables involved makes it clear that dyeing consistent shades is not easy (27).

Even when based on instrumental predictions, most recipes are tested first on a laboratory scale, and are adjusted as appropriate. This is particularly important if any factors, such as the details of the substrate, differ from those used to calibrate the instrumental match system. No laboratory dyeing process can ever completely reproduce the conditions that prevail in a commercial dyeing machine particularly in terms of the agitation developed, and scale up is never perfect.

Considerable effort has gone into making predicted recipes good enough to implement on a commercial scale without first testing on a laboratory scale. An even loftier goal is the concept of "blind dyeing" in which a dyeing process is terminated and the material removed from the machine without first removing a sample and checking the color. Success in either endeavor requires very careful control of all the variables involved, and it should be borne in mind that the calibration dyeings on which the prediction is based should also ideally be conducted on the large scale: a considerable undertaking!

In practice, blind dyeing is still not commonplace, and many practical dyeings are conducted in a way that deliberately undershoots the amount of dye required for a match. At the end of the dyeing process, a check is made and the correct shade achieved by making "an add" (based on spectrophotmetric measurement or a skilled eye) and running the process for an extended time.

Given that dyeings are rarely completely reproducible, the question arises "how close is close enough?" Instrumental color measurement is now capable of making this judgement objectively, and more reliably than the human dye, although getting to this point has taken much effort (28). After the development of the CIELab equation in 1976, some notable improvements in the reliability of equations used to provide quantitative color difference data have been made: the CMC (2:1) equation developed in the 1980s has become the most widely used in the textile world, and has made "single-number shade passing" a realistic concept. Currently, the CIE DE_{2000} equation is being evaluated. Objective passing of shades requires that the customer accept the method, and that dyer and customer agree on the pass–fail tolerance. As the textile supply chain has become global in scale, and the geographic separation between dyehouse and customer has increased, the use of objective shade acceptance has necessarily increased. However, there are still instances when a subjective customer intervenes and all too often tolerances shift with the demand for product. One skill involved in practical dyeing is knowledge of customer preferences and at the same time not wasting resources in getting the color closer to standard than is necessary.

Level Dyeing. A level dyeing refers to one in which dye is distributed evenly throughout the substrate. Strictly speaking, each fiber should be fully and evenly penetrated. This is not always achieved in practice, and often fibers in the middle of a yarn are dyed less well than those on the periphery, and in a fabric, yarns may have pale areas where they cross over each other. As long as the overall appearance is level, such micro-unlevelness is tolerated. In contrast, macro-unlevelness, unless it is a deliberate decorative effect, is not acceptable. This can take many forms, and dyeings may have differential uptake in the form of streaks, spots, crease-marks, as well as more gradual and subtle variations from side-to-side, side-to-middle, back-to-front, or end-to-end of a fabric. Assuming a correctly prepared substrate with no inherent dyeability variations present, levelness relies on the use of the correct procedure based on the substrate, dye selection (using compatible dyes), and the machinery being used and how it might provide agitation, or lead to creasing of the fabric. The heavier the depth of shade and closer to the saturation value for the fiber under the dyebath conditions (pH, electrolyte, etc), the more likely is a level dyeing. Thus for heavy shades relatively little control is needed in the dyeing process, and pale shades are the most difficult to produce level.

Levelness is derived from two alternative scenarios: (*1*) Level initial application of dye and (*2*) Migration (leveling) of dye during dyeing.

Unlevelness is costly and the many possible causes of unlevelness lead to much argument to pinpoint the cause and assign blame. Causes include poor preparation, grease spots, bad dye solution, or insufficient agitation. Occasionally a fabric is created from synthetic fiber yarns that have subtle differences in morphology that cause dye uptake to vary. The unlevelness occurs in stripes (Barre), which is usually ascribed to “Mixed merges” or greige lot numbers.

Fastness. Fastness is the resistance a dye on a substrate has to removal or destruction. In both subsequent industrial processing (finishing, eg) and in ultimate use, a textile might meet a wide variety of agencies that represent a challenge to its chemical integrity or its remaining with the fiber. Fastness is achieved mainly by the selection of the dyes used in achieving the shade. No matter how well they are applied, some dyes have inherently limited fastness properties. In addition, there is a requirement on the part of the dyer that the dyes be applied correctly, particularly in the removal of dye that remains loosely bound to the fiber surface, or (particularly for reactive dyes, where “fixation” is an appropriate term) the removal of unfixed dye at the end of the dyeing process. Subsequent finishing processes should also be carefully controlled, since under the conditions of finishing, dye desorption can take place, and recontaminate the fiber surface no matter how carefully the dyer conducted the dyeing and rinsing steps. Fastness is determined by standard laboratory tests. These are discussed in more detail in section 15 on “Fastness Testing for Textiles”.

No Damage to the Substrate. Prolonged treatment in a dyebath under hot, wet conditions can damage textile fibers. This can include chemical damage that shows up as a loss of tensile strength, poor spinning or weaving performance, or physical changes such as permanent setting in creased conditions. A dyer who makes multiple adds to get closer and closer to a match, or who has to strip and redye a shade risks damaging the substrate.

Efficiency. Dyeing is a commercial process, and a notably competitive one, and success depends on achieving all the above factors (shade, levelness, fastness, no damage) while being as efficient as possible. Efficiency can involve machine time, energy, labor, water, dyes, chemicals, and must also consider environmental impacts of the process. Finding the best process that allows the most efficient and reliable dyeing is another reason why commercial dyeing is a skillful process. For example, holding fewer dyes in stock might be economical, but might make a level, fast or nonmetameric match harder to achieve. Lower cost dyes may save money, but if they are not standardized accurately, or do not form a compatible combination, they may involve the dyer in additional machine time to make adds and/or reprocess the material. Dyes that level well may have limited fastness.

4. Dyeing of Cellulosic Fibers

4.1. Overview. Several cellulosic fibers are available, but cotton is the most common. It comes to the dyer contaminated by natural and added impurities, and requires extensive preparation before dyeing. The fiber's robustness allows for aggressive laundering processes by the consumer that challenge the integrity of a dyeing: The search is thus for good fastness to such challenges. Several different dye types are available for dyeing cellulose. A comprehensive review of the dyeing of cellulosic fibers has been published (29).

Preparation for Dyeing. Cotton (qv) may be made suitable for dyeing in a variety of forms, such as raw stock, yarn, or piece goods. Cotton fibers are coated with natural waxes and pectins, and are contaminated with motes. Raw stock is normally dyed without thorough dewaxing, since the natural waxes aid in subsequent spinning operations. Surfactants are employed to aid the penetration of dyestuffs through the protective waxes. Flaws in the dye levelness are overcome by the mixing that takes place in subsequent carding.

For yarns more thorough treatment is required since auxiliary lubricants may be added during yarn spinning and winding. The waxes can be removed by aqueous alkalies at 80°C or above, and yarns, especially hard-twisted ply yarns that are hard to penetrate are frequently given a kier-boiling (batch treatment in hot alkali solution) prior to dyeing.

Most cotton is prepared and dyed in fabric form. Careful preparation of cotton piece goods is essential to achieve suitable dye penetration, fastness, and general appearance. Fabric construction dictates whether the fabrics will be processed in rope or open-width forms. Heavy piece goods, and those which are subject to rubs and crease marks, are handled in open width. Like dyeing, preparation may be carried out in batch, semicontinuous or continuous processes. For large scale operations, although batch kiers are still used for boil-off and bleaching, they have been replaced largely by steam-heated J-boxes or steamers that allow continuous processing and reduction of processing time, even when subsequent batch dyeing is used.

The first step in open-width preparation of wovens is singeing which burns off lint and fuzz from the fabric surface. The goods are then usually impregnated with a solution to effect solubilization of the sizing applied during weaving. Starch is the most common sizing material and this is removed best with amylase enzymes. Other synthetic polymer sizes such as poly(vinyl alchohol) are removed in hot water with alkali. Alkaline oxidation systems are effective at dealing with a wide range of sizing materials, and are useful when grey goods are obtained from many sources and the type of size used varies. After desizing, woven cotton fabrics are scoured to remove the waxes and pectins. The waxes can be removed by aqueous alkalies at 80°C or above or by solvent treatment. The use of solvents has declined dramatically for environmental and cost reasons. In the last 10 years, interest in enzymes, especially pectinases, in the preparation before dyeing has been extensively examined. However, alkali is still the most widely used scouring method since it can readily be combined with desizing and later bleaching, and it removes motes (seed fragments) that are not readily removed with enzymes.

Before dyeing light or bright shades, the goods should be bleached. Despite its wide use in domestic bleaching, the use of hypochlorite in commercial bleaching is rare today, and bleaching is accomplished with hydrogen peroxide and caustic soda. This operation also helps in the removal of trace impurities that remain after scouring.

Since desizing, scouring and bleaching can all be accomplished with a combination of alkali and hydrogen peroxide, continuous processes can collapse the three steps into two, and given sufficient time, one-stage pad–batch preparation is feasible.

Mercerizing is an optional part of the preparation sequence. It is accomplished by passing the cotton fabric under tension through 15–30% caustic soda, and then rinsing out (and recycling) the alkali. Improved strength, luster and dye uptake result from the permanent changes of morphology from Cellulose I to Cellulose II. Mercerization techniques using liquid ammonia were examined and commercialized in the 1970s, particularly in preparation for cross-linking finishes, but are little used today.

While knitted fabrics do not contain size, they are typically contaminated with knitting oils. These are removed by either alkali treatment or solvents. Once again, solvent treatments are falling out of favor. Where water-immiscible oils have been used and the fabric is to be dyed at 80°C or above, a minimum scour to remove dirt and stains can be sufficient, the rest of the oil being removed during the dyeing process.

Viscose rayon, because of its low wet strength, must be processed under minimum tension at all stages of preparation. Yarns contain few impurities and require only light scouring. Piece goods may contain starch or sizing compounds, which were applied prior to weaving, and may require an open-width enzyme desizing followed by scouring, either in open-width or in rope form, depending on fabric construction and weight. In general, fabrics may be prepared for dyeing by scouring in mildly alkaline synthetic–surfactant solutions.

Since the introduction of lyocell, the tendency of this fiber to fibrillate during wet processing has made its fabrics a significant challenge to the dyer. Essentially, scouring is conducted under conditions that encourage primary fibrillation, and a treatment with cellulase enzymes defibrillates the fabric prior to dyeing. Later, in finishing, secondary fibrillation is encouraged to develop the "peachskin" effect for which this fiber is well known (30).

The Dyeing Process. When cellulose fiber is immersed in water it develops a negative charge, the zeta potential. In order for dyes to show good affinity on cellulose the dyes must be soluble, and have planar, aromatic structures. Solubility is generally achieved via sulfonic acid or other negatively charged groups and the dyes show long-range, Coulombic (ionic) repulsion, but very strong short-range van der Waals forces of attraction. Thus there is a potential barrier that a dyestuff molecule has to overcome. In a static state, assuming no thermal agitation, the ionic concentration varies as in Figure 5(**a**) as the negatively charged molecule approaches the fiber.

Figure 5**b** shows the effects of natural and introduced thermal agitation that tend to equalize the distribution of ions. The differences in profile between Dye^- and Cl^- are due only to the dye exhibiting strong close-range forces of attraction. (*Note:* For simplicity of comparison with Fig. 5**a**, the y axis of **b** is relative, not quantitative).

The use of electrolyte is critical in the dyeing of cellulose. Sodium chloride or sodium sulfate are most often used, although any electrolyte is effective.

4.2. Direct Dyes. The simplest way of coloring cellulosic fibers is with direct dyes. Direct dyes provide reasonably bright shades that cover most of

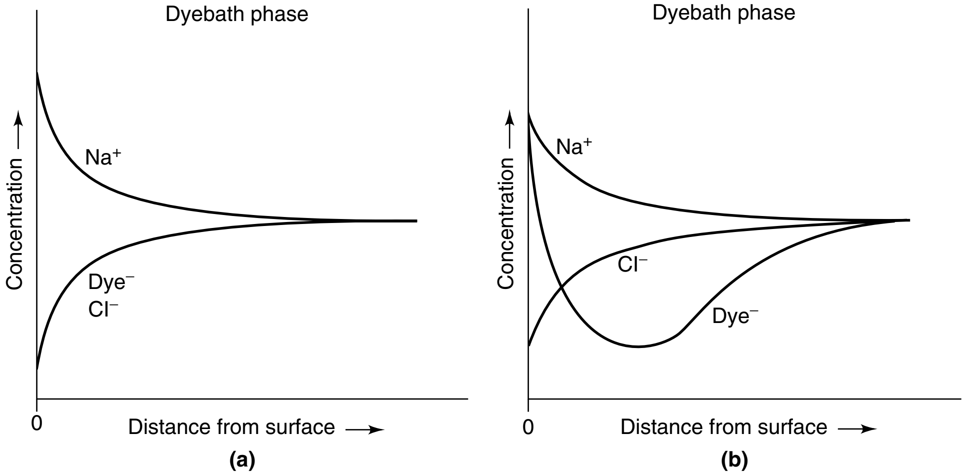

Fig. 5. (**a**) Ionic concentrations in static state. The *y* axis represents the cellulose surface. (**b**) Distribution of ions in practice.

the color gamut. Bright greenish yellows and fluorescent colors are not available. The addition of salt is used to allow dyestuff to be absorbed on the fiber. This is done carefully to ensure that level dyeing is achieved, especially during the early stages of dyeing. The temperature is also controlled throughout the process, both to encourage initial level uptake and later to speed up diffusion, increase the rate of dyeing, and promote migration. If a high affinity dye is being applied then the dyeing process can start without added salt. The addition of a small amount of salt neutralizes the negative surface charge and allows dyeing to continue. However, each dye has negative charges from the sulfonic acid groups in the molecule, and as each molecule of dye is absorbed onto the fiber it increases the fiber's net negative charge that is then neutralized by Na^+. Eventually there is insufficient Na^+ to neutralize this charge, the fiber again develops a negative charge at the surface, and dyeing stops. Further addition of salt allows dyeing to continue. It is therefore possible to control the rate of dyeing by salt addition during the early stages.

Leveling Power. Direct dyes are classified by the CI (6,7) according to their leveling characteristics. Class A direct dyes migrate well and have high leveling power, ie, they have low affinity and high diffusion. They may dye unevenly at first but prolonged treatment at temperatures at or near the boil brings about even distribution. The dyes are applied by adding to the dyebath all the dye and all the salt needed, depending on the depth of shade. The amount of salt added is usually in the range of 5–25 g/L. The dyebath is set at 40–50°C, the cellulose added, and the temperature raised to ∼60°C, and kept there until exhaustion is complete or leveling achieved. These dyes equilibrate rapidly and thus have a low temperature of maximum exhaustion. Leveling is encouraged at higher temperatures, and thus dyeing may be carried out at elevated tempara-ture for a time, and then cooled to allow greater exhaustion.

Class B direct dyes level less well than Class A, and exhaustion must be controlled by careful salt addition. If these dyes are not taken up uniformly in the initial stages it is more difficult to correct the unlevelness. They are dyes that have medium–high affinity and poor diffusion. In their application the cellulose is entered into a dyebath containing only dye. The salt is added gradually and portionwise as the temperature is increased and possibly the final additions made after the dyebath has reached the appropriate temperature, typically $\sim 80^\circ$C.

Class C direct dyes have high affinity where, resulting from the complexity of the molecules, the nonionic forces of attraction dominate and can overcome the ionic repulsion of the surface. They are thus dyes of poor leveling power which exhaust well without added salt and the rate of exhaustion is controlled by temperature.

The division of direct dyes into these classes is based on laboratory tests under specific conditions, and there is obviously a continuum of behavior. Real processes may used different conditions, and the behavior of dyes may vary with conditions. Although the rates of migration vary considerably from dye to dye and with different dyebath conditions, the generalized relationships between Classes A, B, and C tend to hold (31).

Wetfastness. The level dyeing behavior described above reflects the affinity of the different classes of direct dye. Not surprisingly, the same range of affinity leads to different fastness properties of these dyes. Class A direct dyes offer the most trouble-free process for dyeing cellulose. However, they do not always provide sufficient wetfastness. When a dyed textile is placed in a hot solution of water, as is the case in domestic washing, the dye desorbs from the fabric with a tendency toward a reestablishment of the equilibrium between dye in fiber and dye in solution. This happens every time the textile is washed. For Class A, direct dyes their low affinity and high diffusion means that significant amounts of dye may be lost within the times associated with domestic washing. Further, Class A dyes show a high propensity to migrate from dyed fabric to undyed, or different shade, fabrics in the same wash liquors. Being anionic, not only will they stain cellulosic materials, but also nylon, wool, and silk.

The Class B and C dyes show better resistance to desorption, ie, they show higher wetfastness, but they do not overcome it fully, and even the Class C direct dyes show inadequate wetfastness and poor staining of adjacents in more severe fastness tests as a result of the reversible nature of the dyeing process.

The general utility of direct dyes and their relatively simple application processes have made aftertreatments to increase their fastness attractive propositions. A wide variety of treatments was developed for dyes with appropriate functional groups: with the rise in popularity of reactive dyes, such treatments have declined in use. However, the application after dyeing of a cationic surface-active agent to form a sparingly soluble complex with the dye will improve wet fastness slightly, and is still of some use.

4.3. Fiber-Reactive Dyes.

Reactive dyes form the most recently introduced class of dye. Since their invention in the 1950s, their good wet fastness and extensive shade range have made them the dominant dye type for dyeing cellulose fibers.

Reactive dyes provide bright shades that cover most of the color gamut. Bright greenish yellows and fluorescent colors are not available. Light fastness varies with the chromogen, and is good in those dyes based on anthraquinone and phthalocyanine chemistry. Metallized azo reactive dyes also have good light fastness. As well as use in dyeing, reactive dyes are the major class of dye used in textile printing. The environmental issues with reactive dyes have been discussed earlier.

A reactive dye contains a chemical group capable of reaction with cellulose to form a covalent bond. It is absorbed onto cellulose in the same manner as a direct dye, with the aid of electrolyte. In general, reactive dyes are more anionic (and more soluble) and involve the use of greater amounts of electrolyte. When alkali is added, ionization of cellulose and the reaction between dye and fiber is initiated. As the reaction proceeds, dye is removed from the equilibrium between active dye in the dyebath and fiber phases, which is reestablished by the absorption of more dye. The addition of alkali produces both secondary exhaustion and reaction (fixation).

Fiber-reactive dye is also hydrolyzed by reaction with free OH^- ions in the aqueous phase. This is a nonreversible reaction and so active dye is lost from the system. Hydrolysis of dye can take place both in the dyebath and on the fiber, although in the latter case there is a competition between the reactions with free hydroxyl ions and those with ionized cellulose sites. The hydrolyzed dye establishes its own equilibrium between dyebath and fiber which could be different from the active dye because the hydrolyzed dye has different chemical potentials in the two phases. The various reactions taking place can be summarized as in Fig. 6.

At the end of the dyeing process very little, if any, active dye remains: there is fixed dye on the fiber, and hydrolyzed dye in both the dyebath and fiber. Any hydrolyzed dye that remains absorbed by the fiber will tend to desorb (like a direct dye) in subsequent laundering, and negate the benefit of the covalently bonded (and thus fast) dye. Even very small amounts of residual hydrolyzed dye (1–2% of the original amount applied) give heavy stains on adjacent fabrics used in fastness tests. The same forces that promoted initial sorption make the removal more than a simple rinsing process. Removal is a relatively difficult procedure that is a critical part of the total dyeing process. The final steps in a fiber-reactive dyeing are thus a series of rinses that remove first electrolyte and alkali, and then encourage the desorption of hydrolyzed dye.

The chemistry and application processes for reactive dyes concentrate on maximizing exhaustion and fixation without a risk of unlevel dyeing, minimizing the amount of hydrolyzed dye present, and maximizing its rate of diffusion. Once a dye is fixed it cannot migrate and therefore dyeings achieved using

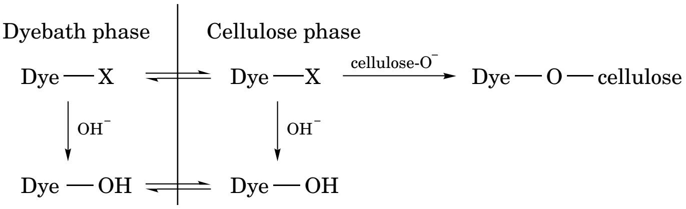

Fig. 6. Reactions taking place in a fiber-reactive dyebath. X represents the leaving group.

fiber-reactive dyes must be level before they are fixed. All this must also be done against a background of commercial considerations of cost and time (productivity), and new reactive types and processes are still being introduced in attempts to improve the overall efficiency of the process (32,33). This applies particularly to the environmental aspects of reactive dyes. In an era when environmental sensitivity prefers natural (cellulosic) fibers, the use of reactive dyes and the high water use in rinsing, plus the high levels of electrolyte required in application, draws attention, and improvements in efficiency are represented by dyes marketed as "low salt" or "low impact" reactive dyes, eg. The inevitable loss of color in the form of hydrolyzed dye has also been noted, and the effluent streams from reactive dyeing are probably the most highly colored. Much research has been conducted on the means to ameliorate this (34), and, since the hydrolyzed dye is not reusable [except, perhaps, as a pseudo-acid dye for a wool or nylon blend component (35)], attention has focused on destruction of the color with, eg, ozone, and recycling the electrolyte in the process (36).

The Ideal Fiber-Reactive Dye Profile. Figure 7 shows the general profile for the application of a reactive dye. In addition to showing the rate profile of fixation between dye and fiber, three other practical parameters (A–C) are noted.

The overall objective is to make the fixation (C) as high as possible for economic reasons. The closer the fixation (C) is to the total dye on the fiber (B) then the smaller the concentration of hydrolyzed material [dye-OH] and the less that needs to be removed in the washing-off process after dyeing.

If the exhaustion with electrolyte and prior to the addition of alkali (A) is low as a result of using dyes with low affinity, then it can be expected that level dyeings will be obtained at this stage. In order for the dye to be economically viable, the secondary exhaustion from the addition of alkali (B–A) must be high. Migration, and hence leveling, is impossible once the dye has formed a

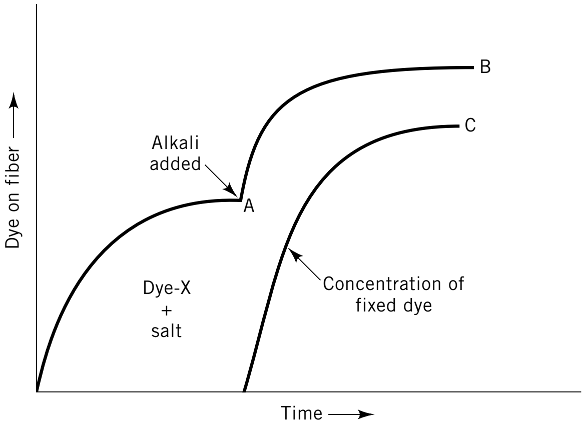

Fig. 7. Amounts and forms of fiber-reactive dye on the fiber as a function of time for a low affinity dye, where X represents the leaving group. Point A represents the amount of dye exhausted in neutral conditions; B is the total amount of dye exhausted at the end of the dyeing process, ie, [dye-OH] + [dye-X] + [dye-O-cell]; and C is the amount of dye fixed [dye-O-cell].

covalent bond with the fiber, thus during the secondary exhaustion phase little migration is possible. Dyes that need a large secondary exhaustion therefore have an inherent risk of unlevelness. This may not be a problem in heavy shades but does become of increasing importance in pale shades. Unlike direct dyes, extending the dyeing time will not improve the situation. Methods of overcoming this problem are to dye at low temperatures when the affinity is at its highest and so increase the neutral exhaustion, and to add the alkali slowly during the secondary exhaustion period to maximize control over and reproducibility of the process.

The ability to dye cold (20°C) or warm (60°C) is often regarded as an advantage because of the energy savings. In order to obtain economic levels of fixation in a practical time period at these temperatures, the rate of reaction between dye and fiber has to be high. These dyes are described as being of high reactivity. A further advantage of these dyes is that because of their low affinity hydrolyzed dye is rapidly removed from the fiber during the washing-off process. However, even with these dyes it is necessary to wash off at elevated temperatures, ideally at or close to the boil.

The extreme alternative is where the initial exhaustion in neutral conditions (in the presence of electrolyte) is high which is achieved by having high affinity dyes. Although level dyeing is more difficult than with low affinity dyes, the advantage is that, resulting from the low secondary exhaustion, little can go wrong after the addition of alkali. The dyeing procedures concentrate on obtaining a level dyeing during the time period before alkali addition by changing dyebath variables, eg, by portionwise addition of salt and dyeing at temperatures in the region of 80°C. Because the fixation is carried out at 80°C dyes of relatively low reactivity can be used. Because these dyes are of high affinity it is more difficult to remove hydrolyzed dye and it is essential therefore that the fixation be as high as possible. As a result of their low reactivity these dyes are not sensitive to hot alkali and therefore it is possible to wash off hot without intermediate cold rinses, offsetting the problems associated with the high affinity of these dyes.

Alkali is usually added in a second stage. However, with low reactivity, high affinity dyes it is possible to add the alkali at the beginning of the dyeing process and control the rate of uptake and chemical reaction with temperature. With high affinity dyes the exhaustion takes place rapidly at low temperature before the chemical reaction becomes significant. If dyes are carefully selected or synthesized to have identical dye uptake it is possible to include all the electrolyte and alkali from the beginning and operate an “all-in” technique.

Application Methods. There are many detailed application methods used for applying reactive dyes, and all have been described in detail (29). Examples of the main methods may be summarized as follows (and assumed are well-prepared goods, and appropriate water quality).

Cold Exhaust Dyeing. Dyeing is commenced at 25–30°C and maintained while dye is added, followed by portionwise addition of salt every 10–15 min, increasing the size of the addition each time among the 3–4 portions. The amount of salt used (10–100 g/L) depends on the depth of shade. Dyeing continues for 15 min after the final addition of salt, then soda ash (10–20 g/L) is added portionwise 15 min. Dyeing continues for 30–45 min. The dyebath is dropped, and a sequence of rinses (cold, followed by several hot rinses) removes all "unfixed" dye.

Warm, Hot Exhaust Dyeing. An isothermal technique for depths of shade >0.5% owf begins at 40°C with salt at pH 7.0. The temperature is brought rapidly up to the dyeing temperature (60–80°C depending on the dye), the dye is added over 10–15 min and the dyeing run for 30 min before adding alkali portionwise over 10–20 min. Dyeing continues for 45–60 min before dropping the dyebath and starting the wash-off sequence.

Migration Exhaust Technique. This is a preferred method for for pale shades (<0.5%owf) of warm–hot exhaust dyeing dyes. Dyeing is commenced at 50°C with salt at pH 7.0. Dye is added >20 min and the temperature is raised to the highest safe level depending on the dye (typically ~95°C with monochlorotriazinyl reactive systems) at a rate of 1.5°C/min. After 20 min at this temperature, the dyebath is cooled to 60–80°C (depending on the dye) and alkali is added portionwise over 20 min. After a further 30 min the dyebath is dropped and the washing sequence begun.

All-in Method. Dyeing starts at 25°C with salt and alkali (mixed soda ash and caustic soda), and runs for 15 min, before adding dyes over 10 min. After a further 15 min the temperature is brought up to 80°C over 45 min and maintained at this temperature for 30–60 min before dropping the dyebath and starting the washing process.

Continuous Dyeing. In this case, the fabric is passed through a trough containing dye solution and then squeezed through a padding nip at controlled pressure. The dyestuff is therefore applied to the fabric by physical means, rather than by exhaustion. The alkali can be added to the system by either premixing it in the dye solution or separately in a second padding treatment. The reactivity of the dye and ambient temperatures dictate whether dye and alkali are applied together in either simple admixture (low reactivity) or by sophisticated dosing techniques (high reactivity), or by a second application process (both). Urea is sometimes added to promote the solubility of dye in these necessarily more concentrated solutions. It also increases the fixation of dye in the later steaming or baking.

Dyes with low to medium affinity are needed in this continuous application. If the affinity is too high then exhaustion of the dye can take place during the few seconds the cloth is immersed in it causing a gradual depletion of the dye concentration, and the subsequently dyed fabric changing shade with time during the run. This is referred to as tailing. If dyes have very low affinity as the fabric is dried after the application of either dye and/or alkali, the water moves to the areas of greatest rate of evaporation, and if the dye has a low affinity it will migrate with the water giving an uneven dyeing.

After dyeing, the fabric is dried quickly to a moisture content below that at which migration can occur and then either steamed or baked (thermofixed), followed by a washing-off process. All the processes run continuously and in tandem, the fabric passing from one process and machine to the next.

Cold Pad-Batch Dyeing. Dye and alkali (eg, 5–30 g/L soda ash or sodium silicate, depending on shade and dyestuff) are padded, and the whole batched for 4–24 h at ambient temperature, the time depending on the dye. As in all other methods a final washing-off process is needed to remove hydrolyzed dye. This application method is of growing popularity because of the increased demand for short yardages to a particular shade which are not economically suited for coloration by continuous methods, the simplicity and low capital cost of the equipment, and the low energy usage. The inability to make "adds" to correct the shade is a limitation to more widespread implementation of this method.

Pad-batch dyeing shows its primary benefits over other methods where it is possible to apply the dye on gray (unbleached) minimally prepared fabric, eg, T-shirts, followed by washing on the same perforated beam used to batch the fabric after dyeing. Where a bleached fabric base is needed, the bleaching is best carried out using peroxide by pad-batch technique in order to ensure an even effect and pick up when padding the dye liquor. Similarly all other preparation is best carried out in open-width.

Chemical Types. A wide range of reactive groups have been investigated, with 20–30 used commercially and >200 patented. These have been described in detail elsewhere (35). Because these reactive groups differ chemically the activation of the reactive systems is different as are the rates of reaction with cellulose, from one reactive system to another. This rate of reaction with cellulose, or reactivity, dictates the temperature and pH needed for dyeing.

The most important reactive groups are those based on halotriazine or halopyrimidine systems, where an activated halogen substituent undergoes a nucleophilic substitution reaction with ionized cellulose, or dyes based on sulfatoethylsulfonyl groups. With dyes containing sulfatoethylsulfonyl groups the group converts under alkaline dyebath conditions to a vinyl sulfone, $SO_2CH{=}CH_2$, group that reacts with cellulose by an addition reaction at the double bond.

For any reactive group, a range of reactivity levels is possible, although some general observations can be made. Variation occurs because the chromogen as an integral part of the molecule can activate or deactivate the reactive group. The deliberate introduction of electron donating and withdrawing groups either into the heterocyclic reactive group or adjacent to it in the dye molecule alters reactivity.

Because of this range of reactivities, and the further possibility of modifying affinity and diffusion by molecular design of the dye chromogen, it is difficult to classify reactive dyes into broad groups the members of which can be used interchangeably. Switching one dye for another manufacturer's in a dyebath formula is risky, and mixing dyes containing different reactive groups requires care. The dyes are usually referred to by trade name rather than any other classification, and despite the major reorganizations that have taken place in the dyestuff industry over the past decade, such trade names have persisted as the principal means of classifying reactive dyes.

Bifunctional fiber-reactive dyes have been developed. Homobifunctional dyes based on two monochlorotriazine groups were introduced as Procion Supra Dyes and Procion H-E Dyes in 1967. More recently the heterobifunctional Sumifix Supra dyes and Cibacron C Dyes have been introduced, making use of two different types of reactive group in each molecule. Other manufacturers have also been active in researching these mixed bifunctional approaches (32,33).

Correlation of Application, Affinity, and Reactivity. Figure 8 correlates fiber-reactive dye application suitability to reactivity and affinity.

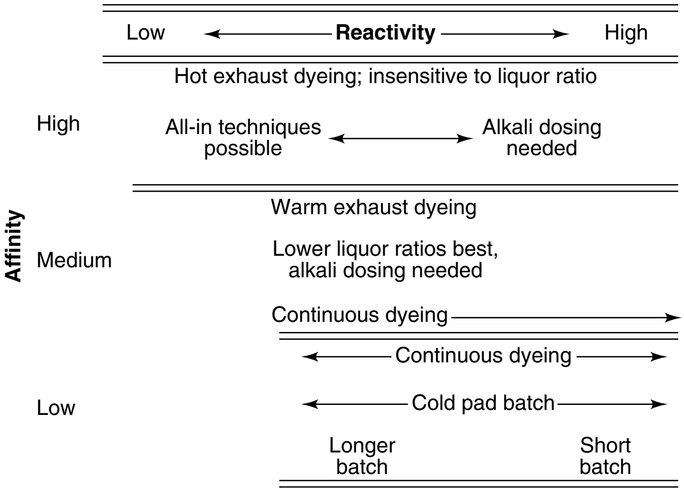

Fig. 8. Summary of dyeing techniques related to dye reactivity and affinity characteristics.

4.4. Vat Dyes.

Vat dyes are are solubilized by reduction with agents such as sodium dithionite under alkaline conditions. The reaction is based on a quinone structure and its $=C=O$ group. In the presence of reducing agents it is reduced to $=CH—OH$, and the dye is rendered soluble with alkali as $=CH—O^- Na^+$.

Reconversion to the original quinone structure of the insoluble pigment is achieved by oxidation, in conjunction with removal or neutralization of the alkali. The dyes are applied by either exhaust or continuous dyeing techniques. In both cases, the process is comprised of five stages: preparation of the dispersion, reduction, dye exhaustion, oxidation, and soaping.

The Process. Preparation of Dispersion. The leuco compound of vat dyes is too air-sensitive to be supplied directly to dyers (cf sulfur dyes), so the reduction is in the hands of the dyer. The reduction is a two-phase reaction between soluble reducing agent and insoluble dye particles, and therefore the rate of reduction is influenced by the particle size distribution of the dye dispersion. The smaller the particle size the greater the surface area, and hence the more rapid the reduction process. Vat dye technology has benefited greatly from the advances in dispersion methods and materials that were necessary for the successful implementation of disperse dyes in the challenging conditions of application to polyester.

Reduction. This was studied in great detail half a century ago (35). The reduction is reversible and an equilibrium between oxidized and reduced forms can be obtained in the presence of a reducing agent. This leads to the definition of a redox potential, the electrical potential in volts obtained at a platinum electrode when there are equal concentrations of oxidized and reduced forms at unit activity of hydrogen ions at 25°C. Products with a positive redox potential are oxidizing agents, those with a negative potential reduce compounds whose redox potential is higher. As vat dyes are applied in their reduced leuco-soluble form it is essential to have a system with a redox potential considerably lower than that of the vat dyes being used to ensure an excess of the reduced form. This is achieved by using alkaline sodium dithionite (hydrosulfite), which is a strong reducing agent with a redox potential well below that of vat dyes. Several other chemicals (eg, sodium borohydride) have been investigated for use with vat dyes, and work to develop electrolytic methods of reduction has been carried out (36). A sufficient excess of reducing agent, and, since the oxidation products of dithionite are acidic, alkali, must be present to maintain the dye in its reduced form throughout dyeing. The degree of agitation (and any concomitant introduction of air) will affect this. The turbid dispersion of the parent dye and the differently colored solution of the leuco compound make the state of the dyebath apparent.

Dyeing. The exhaustion of the negatively charged leuco form of the dye is covered by the general theory already described. Level dyeing can be a problem with vat dyes, since one of the dyer's controls, electrolyte addition, is limited by the high levels of Na^+ present at the start of dyeing from the dithionite and alkali used in the reduction. Their large molecular size provides a high level of dye-fiber attraction, and these strong forces overcome the coulombic repulsion between the dyes in their leuco form and cotton in alkaline baths. Dyeing rates of the leuco compound are high, with the main mode of attraction due to charge–transfer and van der Waals forces. To encourage levelness, the fine dispersion of unreduced dye can be circulated in a batch dyeing machine before the slow addition of the reducing chemicals.

In the batchwise process the temperature can be raised to 80°C to promote levelness providing dyes not sensitive to reductive breakdown are used. In the continuous application method the vat dye is padded onto fabric and dried under conditions that avoid migration, padded with a solution of sodium hydrosulfite and caustic, and then steamed in saturated air-free steam for up to 60 s.

Oxidation. In view of the low redox potentials of vat dyes, this presents little problem. Oxygen, from air or dissolved in the water used for rinsing will accomplish the oxidation of vat dyes, and is used in some commercial processes. For faster oxidation, or for more direct control of the process, it is common to use a solution of hydrogen peroxide or sodium perborate as an oxidizing agent. Similarly, rinsing can remove most of the alkali, but after oxidation the alkali can also be removed by neutralization. Premature neutralization can result in the formation of the water-insouble acid leuco compound.

Soaping. During the oxidation process the vat dye pigment is reformed inside the cellulose. Deposition of the pigment onto the surface of the fiber also takes place which reduces the fastness to rubbing. This surface pigment is removed by soaping at or near the boil. The soaping process also causes a shade change that for some dyes can be quite marked, and the shade of the fabric needs to be stabilized by this soaping treatment. The causes of this are not entirely clear, and two theories have been advanced: that soaping causes crystal growth and produces crystals orientated in such a manner that the main crystal axis is along the fiber axis and the resonating system arranged perpendicular to this axis (37), or that the soaping process preferentially stabilizes a particular crystal form of the vat dye (38). Soaping is not a problem in batchwise dyeing, but in continuous dyeing multibath large soaping ranges are needed to allow for sufficient immersion time to develop the final shade.

Uses. The main characteristic of vat dyes is their excellent fastness to light, water, and other agents, eg, chlorine. Vat dyes are therefore widely used in outlets demanding high lightfastness such as outerwear, furnishings, drapes, etc; high wetfastness and fastness to repeated washing such as workwear; high chlorine fastness such as institutional articles (such as towels); or where general excellent fastness is required as in the case of sewing threads where it is impossible to know the use of final garment they will be used to construct. Vat dyes can achieve a wide range of shades, but there are few bright reds and yellows, and they are particularly strong in the blue, green, brown, and black regions.

Indigo. Indigo is the prototype vat dye, and undergoes the same reversible reduction reaction with caustic and reducing agents such as sodium dithionite (hydrosulfite) to produce a soluble leuco form for dyeing followed by reoxidation to the insoluble form on the fiber. The major difference between indigo and a typical vat dye is the low substantivity of the leuco form of indigo. Even extended times of dyeing lead only to low exhaustions, and it is usual to apply indigo in a series of "dips" in the reduced dye solution. When cellulose is dipped into reduced indigo the fiber quickly absorbs indigo and reaches an equilibrium. At this stage the material is removed from the indigo vat and atmospheric oxygen reforms the insoluble indigotin in the fiber. The fiber is then reimmersed in the indigo vat, more leuco is absorbed, and the process repeated until the desired depth of shade is obtained. Each time the fabric is dipped there is an incremental increase in depth of shade.

The principal use for indigo is in denim where indigo is dyed continuously on cotton warp yarns which are subsequently woven with white cotton weft yarns to give the typical denim look. Special effects such as "stone wash," "ice wash," etc, are obtained by chemical treatments of the dyed fabric, eg, with sodium hypochlorite or potassium permanganate and pumice. The "wash-down" behavior, where the shade reduces during each wash, is achieved by deliberately ring dyeing the yarn by altering the conditions of reduction and oxidation (39). The more penetration of indigo into the yarn the less wash-down, the less the penetration the greater the wash-down.

4.5. Sulfur Dyes.

Sulfur dyes behave in an analogous manner to vat dyes, and are applied in a reduced form that is later reoxidized into an insoluble dye on the fiber. Sulfur dyes are complex sulfur-containing compounds of indeterminate structure. The principal differences between sulfur and vat dyes derive from the greater stability, and lower affinity of the reduced form of the sulfur dyes. This lower affinity is based on the reduced form consisting of smaller fragments and the oxidized dye being large complex, sulfur-linked structures. (In contrast, the reduced and oxidized form of vat dyes are essentially the same size). While they were formerly supplied as solid materials in the oxidized form they are more usually supplied now as a prereduced liquid that eliminates the need to isolate the solid dye at the manufacturing stage. This liquid is added to the dyebath, but to maintain the reduced form during dyeing, the dyer must add further amounts of reducing chemical. The greater stability of sulfur dyes in the reduced form is indicated by the use of weaker reducing agents and alkalis to do this. Sodium sulfide and sodium carbonate are traditionally used. Environmental problems associated with sulfide have meant that manufacturers try to reduce the amounts in the dye supplied, and also that alternatives to sulfide are used by the dyer. A reducing sugar such as glucose is one such example.

Sulfur dyes, despite their tintorial weakness, are cheap. They penetrate heavy weight and tightly woven materials well, and it is comparatively easy to produce level dyeings. They are used on towels, corduroy, heavy twills for work wear, etc. They produce only dull shades in a limited range of colors. They have a notable sensitivity to hypochlorite bleach. If stored in humid conditions, sulfur-dyed cellulose can weaken drastically on storage, referred to as "tendering", what is thought to be due to the formation of sulfuric acid from free sulfur. It can be avoided by finishing the goods under alkaline conditions.

Application. The lower affinity of reduced sulfur dyes is reflected in their application procedure. Salt is used to promote exhaustion, even in the presence of the electrolyte of the reducing system. They are tinctorially weak, so comparatively large concentrations are applied. Dyeing is carried out at 60°C, although higher temperatures are used for black sulfur dyes. At the end of dyeing a rinsing will remove electrolyte and reducing agent, after which the dye is oxidized. The stability of the reduced form corresponds to a greater challenge in the oxidation. Atmospheric oxygen is insufficient, and a chemical oxidant is required. Since the oxidation is essentially a reassembly of a complex molecule, the conditions of oxidation will change the resulting shade and fastness of the dyeing, and should be carefully controlled. Potassium dichromate was the default oxidant, and presumably resulted in some metal-complexation as well as oxidation. Once again, environmental concerns have prompted the search for alternatives. Peroxide would be the logical choice but has some limitations (40). Among the many oxidants that have been examined, sodium bromate catalyzed with sodium *m*-vanadate has become the most widely used. In heavy shades, surface deposits of insoluble dye produce a phenomenon called "bronzing". Like vat dyes, the insoluble surface dye must be removed in a soaping treatment to avoid problems of rubbing fastness.

4.6. Azoic Dyes. In applying azoic dyes to cellulose, the dyer becomes the dye maker, and the (azo) dye is synthesized within the fiber. Azo dyes derive from the reaction between a diazonium salt and a coupler.

The dyes are especially strong in the orange/red/bordeaux shade area, and since they are insoluble, tend to have good wet-fastness. Light fastness is also good in dark shades and thus they are a traditional complement to vat dyes that are weak in the bright red shades. Like sulfur dyes, they are good for penetrating heavy materials like toweling. They are economical, but they have tended to be replaced by reactive dyes.

Application. The coupler is often referred to as a "naphthol" (since many couplers are hydroxynaphthalene derivatives), and these dyes are thus sometimes referred to as "naphthol dyes". The coupler is applied first. Some couplers are substantive and can be applied in a batch exhaust process somewhat like a very low affinity direct dye, with the aid of electrolyte. More usually the coupler is applied by a padding step, and the fabric dried. At this stage, the fabric is somewhat sensitive to light and chemical fumes, so care and minimal delays are appropriate. The fabric is passed into a bath of the diazo component. The diazo component can be prepared by the dyer's diazotizing an aromatic amine (referred to as a "fast base"). The reaction requires low temperatures, which leads to another colloquial name for these dyes as “ice colors”. More usually, a stabilized diazonium salt is supplied as a “fast salt” and simply dissolved. Depending on the coupler and diazonium salt, buffers are added to control the pH and provide the best reaction conditions. The reaction is virtually instantaneous at room temperature, and the dye is created. Like vat dyes, the final dye is insoluble, and any dye formed on the surface of the fabric must be removed in a soaping treatment to avoid crocking problems.

5. Dyeing of Wool

5.1. Overview. As a widely used fiber before the introduction of the many manufactured fibers, and being a complex material, the dyeing of wool has been widely studied. A comprehensive review has been published (41). The criteria for the selection of dyes for wool have been reviewed (42).

Preparation for Dyeing. Raw wool must be cleaned before it can be efficiently carded, combed, otherwise processed, or dyed. Loose wool, as obtained from the sheep, contains 30–80% impurities consisting of wool grease, dried perspiration (suint), dirt, seeds, and burrs. Methods of scouring the wool vary widely, depending on the type of wool and the amount and types of soil. The equipment for washing wool by the countercurrent method usually consists of four to five bowls in sequence, each 1 meter deep and fitted with perforated trays that support the wool. Forks keep the wool moving along toward heavy squeeze rollers that are located at the end of each bowl and are designed to squeeze out dirty liquor before the wool is passed on to the next bowl. Soap and soda ash, historically used for wool scouring, largely have been replaced by nonionic surfactants: In order to prevent harshening of the wool, soda ash concentrations are kept to a minimum. Scouring temperatures are normally 45–60°C, depending on the system and type of wool to be cleaned. The lanolin recovered from the wash liquors is a valuable by-product.

Wool can be dyed as loose stock; indeed a greater proportion of wool is dyed in this form than other fibers. It can also be spun into yarn and woven or knitted into fabrics, and these require additional preparation before dyeing. Yarns are scoured to remove spinning oils in mildly alkaline detergent solutions. Fabrics are also scoured, to remove knitting oils, or (for woven fabrics) weaving size and dirt. Scouring can be combined with the milling process that compacts the fabric structure since both involve a mechanical action in aqueous conditions. Raw wool scouring does not remove vegetable matter, and wool fabrics thus contaminated require carbonizing. The fabric is saturated with dilute sulfuric acid (3–4% is usual) and then baked. Cellulosic vegetable matter is carbonized to a friable state, and is beaten out as dust from the fabric. The acid that remains on the wool may be made use of in subsequent dyeing and finishing processes. Wool fibers and fabrics are settable under hot wet conditions, and woven fabrics are prone to acquire permanent creases if dyed in rope form. To avoid this, fabrics may be “crabbed” before dyeing by passing them in flat form through boiling water. The fabrics are thus set in a flat condition, and resist the setting of creases.

Dyeing Mechanism. Wool (qv) is a complex protein polymer based on some 20 amino acids. The polymer chains are cross-linked by disulfide groups of cystine, and the presence of aspartic acid, glutamic acid, arginine, and lysine leads to the presence of amino and carboxylic acid terminated side chains, as well as at the chain ends.

5.2. Acid Dyes.

These form the most widely used group of dyes for wool.

Classes. In a manner parallel to the direct dyes, the acid dyes form a large group that it is convenient to break into smaller groups that have similar dyeing and fastness behavior. Among the dyes that are not involved with metal complex formation three classes of acid dyes are usually recognized in wool dyeing: acid leveling, acid milling, and super milling or neutral dyeing.

Acid Leveling Dyes. These are molecular dispersions at low temperatures (true solutions) and are simple molecules. They have low affinity at neutral pH but exhaust well at acidic pH when the wool becomes charged and ionic bonding contributes. They exhibit good leveling and migration behavior. Their low affinity also results in low fastness. In many cases, wool is not subjected to severe wet treatments after dyeing, and thus this lack of fastness is of less consequence than it is for direct dyes on cotton.

Acid Milling Dyes. These are colloidal dispersions at low temperatures and true solutions at high temperatures. They are generally larger molecules than acid leveling dyes and have a higher nonionic attraction. These dyes have medium fastness and medium leveling, migration, and fastness properties. Their name derives from their fastness when applied to wool that is subsequently milled as part of its finishing sequence.

Super Milling Dyes. These are colloidal dispersions at both low and high temperatures and are complex molecules that often contain hydrophobic alkyl chains that increase attraction through van der Waals forces, charge transfer, and hydrophobic interaction, and thus enhance fastness. These dyes exhibit high affinity at neutral pH. They exhibit high affinity and high fastness but poor leveling and migration.

Controlling Dyeing Behavior. As with all other dyes the dyeing process concentrates on obtaining level dyeings within an economic time period, and once again slower dyeing means better control and level dyeing is enhanced. When dyeing wool with acid dyes four factors control the dyeing behavior: pH of the dyebath, presence and concentration of electrolyte and/or leveling agents, temperature of the dyebath, and choice of dyestuff class.

Effect of pH. The simple acid leveling dyes exhibit little affinity for wool with a net neutral charge (ie, at ~pH 4–5). When wool is charged the dye is absorbed by ionic attraction, until the negative charges taken onto the wool by the charged dye neutralize all the charges, and then dyeing stops. The lower the pH the more positive sites on the wool and an excess is needed to obtain full exhaustion in deep shades. This is achieved at ~pH 3.0 by using dilute sulfuric acid. The dyes are mobile, and as their name suggests, even initially unlevel dyeings can be leveled by prolonged treatment. The behavior of these dyes would be represented by curves A and A′ of Figure 3.

Acid milling dyes have medium neutral affinity and dyeing can commence on neutrally charged wool. If excess positive charges exist then rapid absorption and unlevel dyeing result. Usually acetic acid is sufficient to generate the requisite number of sites. Migration of dye is limited, and the leveling of unlevel dyeings is slow: behavior woud be represented by curves B and B′ of Figure 3.

Super milling dyes have a high affinity for neutrally charged wool and the rate of dyeing is sufficiently high without any acid in the system to require control to give level dyeing behavior; indeed, at the neutral pH values used, wool is slightly negative and ionic repulsion is used to slow the dyeing rate. The aim is to have a minimum initial rate of dyeing. An acidic pH is needed to achieve full exhaustion and this is obtained by using acid generators, eg, ammonium acetate, that cause the pH to drift increasingly acidic during the dyeing process.

Electrolyte and Leveling Agents. The usual electrolyte used is sodium sulfate. The sulfate ion, SO_4^{2-}, has a low affinity for the wool, but because of its smaller size exhausts onto the sites before the dye. As the dyeing process progresses the higher affinity dye molecule displaces the sulfate ions. The sulfate ions therefore slow down the overall rate of dye uptake, and act as “retarders”. The degree of retardation of the dyes depends on the importance of ionic attractions and the affinity of the dye for neutrally charged wool. the retardation effect is most effective with acid leveling dyes. It is less with milling dyes, and the presence of sodium sulfate may cause problems by increasing aggregation of dye and the temperature at which the aggregates break down: Rapid disaggregation at higher temperatures can lead to an unlevel strike that is difficult to level out. In the case of the super milling dyes the effect of electrolyte as a competitor for dye sites is minimal. Methods that use sodium sulfate to maintain the dye in aggregated form throughout dyeing, from which dye is slowly released to dye the fiber have been suggested. A variety of leveling agents for wool dyeing have been used. These are usually surfactants. Anionic materials act as competitors for the dye sites, and are more effective than sulfate ions in competition with dyes of higher affinity. Amphoteric or mildly cationic leveling agents are thought to form complexes with the dye from which dye is gradually released to dye the fiber. These agents may also modify aggregation of dyes and prevent rapid disaggregation.

Temperature. No dye transfer takes place <40°C, above which, because the fiber swells, the rate of dyeing increases. For full penetration of the fibers, the dyeing temperature is usually at or close to 100°C. This can be reached rapidly with the acid leveling dyes, but the rate of temperature rise for milling and supermilling types is usually slower to encourage level sorption.

Practical Processes. With acid leveling dyes no real problems exist because the dyes show good migration. Dyes are applied at approximately pH 3, electrolyte is added from the beginning, and rather like Class A direct dyes level dyeing is achieved by prolonging the times at the boil.

The other extreme is found with super milling dyes when at the start ammonium acetate, sulfate, or an organic ester is present without any electrolyte. Dyeing is carried out more slowly taking some 60 min to reach the boil, and often the dye is applied with a leveling agent.

Acid milling dyes are intermediate in behavior being applied with acetic or formic acid in the presence of sodium sulfate.

A disadvantage of acid leveling dyes is that their wetfastness depends on the formation and maintenance of a salt linkage between the charged wool and dye.

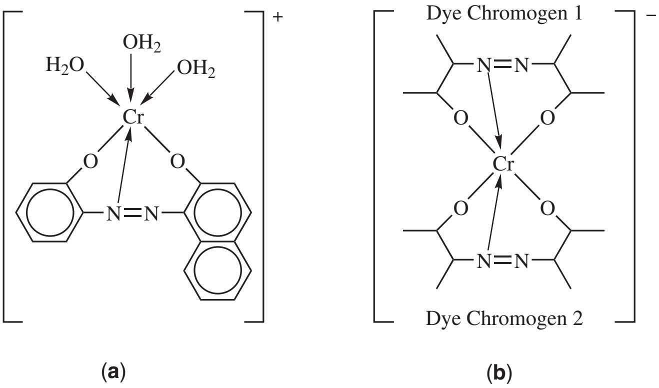

Fig. 9. Chemical formulas for metal complex dyes: (**a**), 1:1 complex; (**b**), 1:2 complex.

A disadvantage of acid leveling dyes is that their wetfastness depends on the formation and maintenance of a salt linkage between the charged wool and dye and is thus dependent on the pH of subsequent wet treatments.

Based on the model of dye–metal ion interaction inherent in the application of mordant dyes, certain acid dyes are produced that involve the chelation of one or more dye molecules with a metal atom during the manufacturing process. The most common metal is chromium, although cobalt is sometimes used.

Two distinct classes of metal complex acid dyes are produced according to the ratio of metal cation to dye molecule anion: 1:1 metal dye complexes comprise one metal cation and one chromophoric ligand (see Fig. 9**a**) and 1:2 metal dye complexes (see Fig. 9**b**) comprise one metal cation and two chromophoric ligands.

5.3. Metal Complex Dyes. The greatest interest is in the monosulfonated dyes. With these dyes the mode of attraction is by the lone pair of electrons on the nitrogen groups in wool acting as a ligand and coordinating with the metal in the dye. This provides both excellent fastness and poor level dyeing properties and migration. In order to control levelness it is necessary to control the availability of the lone pair of electrons on the secondary amine groups. This is done by protonation, but because the secondary amines are weak bases, a pH of 2.0 (obtained by using 8%owf H_2SO_4) is needed. Dyeing is carried out at the boil to enhance levelness, and once finished the act of rinsing increases the pH and reforms the secondary amine groups allowing fixation to take place *in situ*. At these high temperatures and low pH, damage to the wool surface can occur, but the resulting dyeing is of excellent fastness. To avoid the damage associated with application at such a low pH, different ligands have been employed to interact with the chrome, and processes using sulfamic acid have been developed.

1:2 Metal Complex Dyes. With 1:2 metal–dye complexes the coordination number of the metal is fully satisfied so no reaction can take place with the amino groups in the wool. In practice there are three types: (*1*) unsulfonated dyes containing SO_2NH_2 or SO_2CH_3 groups only; (*2*) monosulfonated dyes where the two dye chromogens used are different, one containing a sulfonic acid group, one without; and (*3*) disulfonated dyes. The unsulfonated types have good migration properties, but lowest fastness: disulfonated dyes have poor migration behavior but excellent fastness, and their ease of manufacture makes them the most economical. They are widely used for heavy shades such as navy, black, brown, bordeaux, etc.

The 1:2 metal complex dyes are dyed under conditions very similar to those used for the supermilling (unmetallized) acid dyes. Indeed, manufacturers will often combine the two types into one range that concentrates on the metal complex dyes and uses the supermilling dyes for brighter shades. Thus they are applied either at neutral pH or with ammonium acetate, and the exhaustion achieved by the effect of van der Waals forces. The pH is then allowed to go slightly acidic to form salt linkages between the dye anion and the protonated primary amine groups in the wool (NH_3^+). All the dyes have similar dyeing properties. The use of a slightly lower pH is preferred to minimize wool damage, and auxiliaries to allow the application of these dyes at pH 5 have been developed.

5.4. Mordant Dyes. Many natural dyes were mordant dyes. Given the few dyes available, the range of shades was extended by using different metal salts as mordants. As synthetic analogs were introduced, a wide range of colors could be produced by varying the dye molecule, and the choice of mordant centered on chromium, so while the CI refers to “Mordant Dyes”, “Chrome Dyes” is the more usual term. The application of mordant dyes is essentially the formation of metal–dye complexes during the dyeing process: It is thought that 1:2 complexes predominate. When mordant dyes are applied today, it is almost invariably with the afterchrome (or “topchrome”) method. The dye is applied to the fiber in a process very similar to the application of an acid milling dye: the pH may be lowered at the end of dyeing to maximize exhaustion. Dichromate is then applied from the same bath. The afterchroming process causes a severe color change, which makes shade matching difficult. The process (and thus mordant dyeing in general) is therefore usually reserved for standard repeating shades, especially black, navy and bordeaux.

Since they are formed *in situ*, there is a degree of mechanical entrapment, and the fastness of these dyes is generally better than obtained with the metal complex (or premetallized) equivalents. Chromium, especially Cr(VI), is toxic to the environment and modifications to the process that minimize the level of chrome in the effluent have been the subject of many investigations (43,44). Nevertheless, chrome dyeing is falling in popularity despite the economic and fast dyeings it produces.

5.5. Fiber-Reactive Dyes for Wool. Wool and other protein fibers are replete with groups capable of undergoing reaction with reactive dyes. However, fiber-reactive dyes are by no means as popular for dyeing wool as they are for cotton. They do provide the means of obtaining shades that are both bright and fast: Other fast dyeings on wool (from 1:2 metal complex dyes or chrome dyes) are dull. Such bright and fast shades are required less than on cotton because wool is rarely subjected to more than mild laundering conditions. The exception involves wool that is treated with a resin to render it washable without undergoing the severe shrinkage (felting) that untreated wool suffers: the most common commercial resin is “Hercosett”, and this has become a colloquial name for wool fiber thus treated. Reactive dyes have some difficulties inherent in their application. The need for high temperatures to penetrate the wool scale structure means that dyes of low reactivity must be used to allow absorption before reaction. Wool's sensitivity to alkali also precludes the use of higher pH to promote the reaction and to wash off unfixed dye. The shrinkproofing resin is cationic and promotes a rapid strike of dye, so that levelness can be difficult to achieve.

The dyeing mechanism has been described in detail elsewhere (45). The constraints have led to special groups of reactive dye to be developed for wool.

5.6. Silk. Because it is also a protein, silk can be dyed in the same way as wool, and acid dyes are typically used. Basic dyes have also been used satisfactorily, but only succeed because much silk is only dry cleaned. The term "washable silk" was introduced to cover situations where the dyes used have normal levels of fastness to wet treatments. Like wool, dye application is also at relatively high temperatures, although a full boil is not usually required. Care must be taken to avoid abrasion and chafing during the process: these can raise fibrils that give fabrics a frosty appearance.

Preparation. The main difference between wool and silk is in the preparation of the fiber for dyeing. Silk in its raw state is coated with sericin. It is necessary to remove this gum in order to develop the silk luster and dyeability. Historically, 25–30% soap on weight of fiber (owf) was used for degumming. Synthetic detergent systems, such as higher alcohol sulfates, and soda ash and boric acid have replaced soap to a large extent. Buffered alkalies, especially polyphosphates, are frequently used with synthetic detergent systems. Strongly alkaline systems must be avoided to prevent attack on the proteinaceous silk fibers.

6. Dyeing of Synthetic Polyamides

6.1. Overview. Nylon is synthetic, it has defined chemical structure depending on the manufacturing process, and it is hydrophobic (see POLYAMIDES, FIBERS). The subject of dyeing synthetic polymer fibers has been the subject of extensive review (46,47).

The majority of nylon is either nylon 6 (polycaprolactam) or nylon 6,6 [poly(hexamethylene adipamide)]. Type 6 has a lower melting point, and is generally processed (heat set and dyed) at slightly lower temperatures. A given dye will generally build up more readily and show superior leveling performance on nylon 6 than on nylon 6,6, but have a better wetfastness on nylon 6,6 than on nylon 6. As manufactured fibers, polyamides (nylons) generally require much less preparation than natural fibers that are contaminated with impurities that reflect their agricultural origin. They are usually given an alkaline scour and, since they are thermoplastic, given a heat setting treatment to maintain dimensional stability in the subsequent dyeing. The heat-setting treatment is conducted at $\sim 10^\circ$C above the subsequent wet processing steps; this ensures good form retention after processing. Woven fabrics are usually heat-set on a contact heat-setting machine and nylon tricot is generally heat-set on a tenter frame or in steam chambers.

When bleaching is required, sodium chlorite is preferred as the bleaching agent. However, for economy of operation, bleaching is often accomplished with peracetic acid in the alkaline scouring operation. Cotton–nylon blends are frequently bleached first with hydrogen peroxide to remove cotton motes, and sometimes are bleached further with sodium chlorite. Bleaching is followed with an antichlor treatment, involving chemicals such as 0.1% sodium bisulfite and 0.15% tetrasodium pyrophosphate.

Scouring may be conducted on jigs, boil-off machines, or kettles, depending on fabric weight, construction, and crease tendency in the rope form. A combination of a synthetic detergent and soda ash is usually used and scouring is conducted at 85–100°C. Certain nylon blends may require less stringent conditions and the use of less alkaline builders, such as tetrasodium pyrophosphate.

Nylon is prone to physical and chemical variations that affect the dyeing of the fiber. Physical (morphological) differences arise from the "heat history" of the polymer, and occur in fiber spinning, yarn texturizing and fabric heat setting. These affect the application of all dye types, with the differences generally being greater with dyes of larger molecular size. Chemical differences involve changes to the amine groups present and arise from oxidation, in bleaching, for example. These variations only affect dyes that interact specifically with amine groups, most notably acid dyes. Physical and chemical variations will affect the rate and extent of dye uptake and a nylon fabric will tend to dye unlevel if it contains fibers with these variations. Diagnostic tests are available for assessing physical and chemical variation (48).

6.2. Acid Dyes. Many of the same acid dyes that are applied to wool are also used on nylon, and since nylon is more widely used than wool, nylon now represents the major outlet for the use of these dyes. The same range of types exist, ranging from the easier-to-level, lower fastness to the higher fastness dyes prone to unlevelness, but the groups are named differently, and often dye suppliers will have their own demarcations. A commonly used way of dividing acid dyes on nylon is into Groups 1, 2, and 3, roughly corresponding to Acid Leveling, Acid Milling, and Supermilling dyes for wool. Group 1 includes dyes with little affinity at neutral or acidic pH, but that exhaust under strongly acidic conditions: as mentioned previously, nylon is susceptible to damage at low pH, and a higher pH is used with these dyes on nylon than on wool. Group 2 is the largest group of dyes, which exhaust onto nylon in the pH range 4.0–5.0; and Group 3 dyes have a high affinity for nylon under neutral or weakly acidic pH. Only dyes within one group should be used together, and dyestuff manufacturers assist in this by having different nomenclature for dyes in each group. In contrast to wool, where the tendency is to dye at constant pH, the use of a sliding pH to control exhaustion while achieving levelness is common in nylon dyeing. The usual methods of dyeing are described below, but in the 1990s efforts were made to commercialize a patented process by which dye was metered slowly into a dyebath held at pH and temperature conditions where exhaustion was quite rapid. The process gave level dyeings with only partial penetration of individual fibers (49).

Tanning Agents. The wetfastness of acid dyes can be increased by after treatment. The original method was to apply tannic acid and tartar emetic (potassium antimony tartrate) in a sequential process under slightly acid conditions. An insoluble complex was formed on the fiber and essentially blocked the "pores" through which dye can desorb. The method is long and time consuming and the complex itself is slightly colored which dulls the shade pastel colors. Antimony is also environmentally questionable. Today synthetic tanning agents (syntans) are used. These are anionic phenolic condensates that have a similar effect, although they do not improve the fastness quite as much as the classic treatment. Being anionic they are applied from a treatment bath at pH 3–5. They similarly inhibit diffusion of dye out of the fiber: similar chemistry is used to provide "stainblockers" that prevent the absorption of stains in nylon carpet fibers. Some recent research has examined ways of using a tannic acid complex without the use of antimony salts (50).

Metal Complex Dyes. The 1:1 metal–dye complexes cannot be used on nylon as they are on wool because the low pH values needed cause fiber degradation: However, some of these dyes can be used satisfactorily at higher pH values. The 1:2 metal–dye complexes are more widely used. They have excellent lightfastness in pale shades, and provide the main way to achieve dark dull shades, especially black. These macromolecules are difficult to apply level in pale shades and are sensitive to both chemical and physical variations. Where strict environmental controls are in place, even the chrome complexed within these dye molecules is of concern, and alternatives are sought. In their application they are treated as the Group 3 acid dyes.

6.3. Other Soluble Hydrophilic Dyes. Although nylon is a hydrophobic fiber, water-soluble dyes diffuse into it to a greater or lesser degree. Nylon also contains both positive and negative sites, and sites that can form the basis for coordinate bonds. Some direct dyes have profiles on nylon very similar to Group 3 dyes, and therefore, to supplement the range of shades available they are sometimes applied with those dyes, and Some dyestuff manufacturers give these selected direct dyes the same nomenclature as their Group 3 acid dyes. Some nylon is produced with anionic sites for which basic dyes are used: These are referred to as "basic-dyeable nylon". Used in conjunction with regular and deep-dyeing nylon, multicolor patterned effects can be achieved in a single dyebath. In view of the search for increased fastness, the possibilities of using reactive dyes to react with amine groups in nylon has been examined. In general, the number of amine groups on normal nylon is insufficient, and the irreversibility of the process makes it imperative to ensure that the fiber does not suffer from any chemical or physical variation. Most recently, a modified nylon and a range of specially developed reactive dyes were promoted (51). The generally good dye uptake of all anionic dye types by nylon is also shown be recent interest in the use of sulfur dyes on the fiber (52). The same research group has also examined the possibilities of using vat dyes.

6.4. Disperse Dyes. The insoluble, hydrophobic disperse dyes readily dye nylon, and because their mode of attraction is completely nonionic they are insensitive to chemical variations. Small molecular-sized disperse dyes ($\sim$mw 400) of the type originally developed for acetate show very high rates of diffusion and excellent migration properties and they are insensitive to physical variations in the nylon. As the molecular size of disperse dyes increases they show increasing fastness, but at the same time, greater sensitivity to physical variation.

Although disperse dyes are readily absorbed at temperatures up to the boil, they are also readily desorbed. The glass-transition temperature of the fiber is exceeded at normal laundering temperatures, and desorption into an external aqueous phase is readily possible. Of all the types of dye for nylon, they exhibit the lowest fastness properties. There are no known methods of overcoming this problem although at one time disperse dyes containing fiber-reactive groups were commercially available. As on acetate, some blue disperse dyes on nylon suffer the problem of "gas-fume fading".

The main use for disperse dyes is where excellent coverage of fibers likely to have physical and chemical variations is needed, and where wetfastness is not critical. The small molecular weight dyes are therefore widely used for pale shades on continuous filament yarns used in hosiery. There is also some use made in exhaust dyeing of carpets made from continuous bulk filament nylon to give good coverage. The higher molecular-weight disperse dyes are not of importance on nylon because of their poor fastness and poor coverage of physical variations, and the use of the smaller molecular weight dyes is declining in favor of faster acid dyes as the amount of fiber reaching the market with physical and chemical variation has declined.

Dyeing is relatively simple. The disperse dye is added to a dyebath containing a nonionic dispersing agent, sodium hexametaphosphate, and sometimes acetic acid is added to give pH 5.5 to prevent decomposition of some disperse dyes. Dyeing is carried out by bringing the dyebath to the boil, and continuing until exhaustion is completed.

6.5. Carpet Coloration. Some 50% of all nylon is in the form of carpets almost exlusively colored with acid dyes, and ~50% of the carpet manufacturing industry is located in the United States. The acid dyes from Group 1 are those most widely used because they exhibit the rapid diffusion needed to penetrate the bulky yarns used in carpets, especially bulk continuous filament yarn used in tufted constructions, with high exhaustion. Their wetfastness properties are generally adequate for most outlets.

The most popular coloration method is to apply the dyes continuously, usually by padding, but printing, spray jet, and droplet applications are used. In order to obtain patterned effects, chemical or physical resisting agents can be applied first, and deep and normal dyeing nylon and basic dyeable nylon blends can be used. In the latter case the basic dyeable nylon is dyed with cationic dyes. Carpets can be printed in an analogous method to other textiles and this process is more popular in Europe than the continuous application techniques used in the United States.

The acid dyes are applied with strong acids, eg, sulfamic acid , to give the low pH needed to give an adequate number of $—NH_3^+$ groups for rapid and high exhaustion. After physically applying the dyestuff the carpet is usually steamed wet, its bulk making drying difficult and expensive, for 5–8 min at 100–105°C. After, steaming, the carpet is immediately washed to remove unfixed dye and auxiliaries. Alternatively, the carpets can be batch dyed on the winch, starting neutral and slowly adding acid over a period of time to promote exhaustion. This is known as the "pH-swing method" and is relatively popular in Europe.

Where high wetfastness is needed, eg, in hotel lobbies and bars where liquid spillages are likely, the higher fastness acid dyes (Groups 2 and 3) and even metal complex dyes are used.

7. Dyeing of Acrylic Fibers

7.1. Overview. Pure poly(acrylonitrile) is not an interesting fiber and it is virtually undyeable. In order to make fibers of commercial interest, acrylonitrile is copolymerized with other monomers such as methacrylic acid, methyl methacrylate, vinyl acetate, etc, to improve mechanical, structural, and dyeing properties. Fibers based on at least 85% of acrylonitrile monomer are termed acrylic fibers; those containing between 35–85% acrylonitrile monomer, modacrylic fibers. Modacrylic fibers tend to contain vinyl and/or vinylidene chloride among the comonomers: the chlorine provides the fibers with a degree of nonflammability. Acrylic and modacrylic are in general dyed similarly, although the type and number of dye sites generated by the fiber manufacturing process have an influence (see FIBERS, ACRYLIC).

Acrylic fibers can be produced both by wet and dry spinning methods. This, together with the variation provided by the amount and type of comonomers, means that acrylic fibers vary more from manufacturer to manufacturer than other fiber types. Because of the wool-like end-uses (eg, sweaters, socks, blankets) in which the fiber found use, some early versions included basic comonomers that rendered them dyeable with acid dyes. These are now obsolete. Instead, most acrylic fibers now contain anionic groups which means that basic dyes are the most popular class applied to acrylic fibers. The anionic groups may be those derived from the polymerization initiator, and/or those from the comonomers used: the former are stongly anionic, usually $—SO_3^-$, while the latter can be strong or weakly anionic carboxylic acid groups. If they are carboxylic acid groups, the charge on the fiber is pH dependent and thus under the control of the dyer. The type and number of anionic groups, plus the openness of the fiber derived from the spinning method means that many different acrylic fiber variants are possible. Like nylon, acrylic can be dyed with disperse dyes. While the fastness is a little better, the saturation values can be low. Disperse dyes are therefore only used for pale shades where excellent levelness is needed: Levelness of pale shades with basic dyes is a challenge, so for these cases the disperse dyes are occasionally quite useful.

The “site” nature of the dye–fiber interaction means that the Langmuir isotherm best describes the absorption behavior of basic dyes. This implies a saturation based on the number of sites, and because the potential dye sites are introduced deliberately their number differs from fiber to fiber. In order to compare different acrylic fibers, the saturation value for a fiber has been defined as the %owf of a basic dye of mw 400 that occupies all the available (those in the amorphous regions) sites in the fiber. Commercial fibers have saturation values that vary from ~1.2 to 3.5%, a factor of almost 3 (46,47).

7.2. Preparation for Dyeing. Fabrics are scoured with a synthetic detergent at 45–65°C and are rinsed before further processing to remove tints, size, wax, grease, spinning oils, or other impurities that were applied or picked up during the manufacturing operation. Bleaching, when required, is usually accomplished by means of a sodium chlorite bleach, a selected optical brightener, or a suitable combination of the two. Acrylic-blend fabrics may require other bleaching agents if chlorine-sensitive fibers are present. Most acrylic fibers require a presetting in open-width in boiling water to avoid dimensional stability problems during subsequent wet-processing steps.

7.3. Level Dyeing. *Compatibility Values.* The problems of level dyeing and the need to apply dyes in admixture to give more shades necessitates a way of measuring the compatibility of basic dyes. Depending on charge, the degree of localization, and molecular shape and size, dyes have different affinities and behavior and hence different dyeing rates. A qualitative testing procedure has been defined (53) to assign compatibility values on a 1–5 scale based on comparison with dyes of known properties. In combinations, the dye with the lowest value exhausts most rapidly. For best results dye mixtures should consist of dyes having the same compatibility value, or at least no more than one value different. Anionic and cationic leveling agents can alter compatibility values.

The compatibility value is mainly related to the affinity of the dye for the particular fiber. Because there is little possibility for migration this does not play a significant part in determining compatibility. The rate of dyeing of a specific mixture of dyes of the same compatibility value is not determined by the value itself. The adsorption of cationic dyes is influenced by the presence of others in the dyebath; the presence of cationic retarding agents and electrolytes also influences the rate of exhaustion. It is therefore possible to have a combination of dyes with a compatibility value 3 that under specific dyebath conditions exhausts more rapidly than a combination based on dyes of compatibility value 5.

Techniques. It is exceptionally difficult to obtain level dyeings on acrylic, and temperature and pH control depend on fiber type and are not always adequate. Sodium sulfate is usually added: The salt behaves in the same way as it does in direct dyeing on cellulose, but with opposite effect. The negative surface charge is similarly neutralized, but in this case the rapid strike of dye at the surface is slowed.

Anionic retarding agents can be used, where a dye–agent complex is formed. The breakdown of this takes place slowly as a function of temperature, so limiting the availability of the dye chromogen anion and therefore promoting slow rates of dyeing and levelness. The disadvantages of anionic retarding agents are that they behave differently with different dyes and can produce incompatibility, they reduce the final dyebath exhaustion, and they do not affect the availability of sites on the fiber and therefore do not exert total control over the system. The solubility of the dye–retarder complex can be low, and to prevent its precipitation a nonionic agent is typically used in conjunction with the anionic material.

Cationic products are popular method for the control of leveling. Higher molecular weight cationic products form a surface blocking effect that slows strike and subsequent diffusion into the fiber. Lower molecular weight cationic agents act as colorless dyes that compete with the colored cationic dye for the fiber sites: These occupy sites and thus may modify the effective saturation value of the fiber. If amounts of colored modified basic dye and colorless modified basic dye equal to the saturation value of the fiber are uniformly dissolved in the dyebath then level dyeing behavior is promoted. In practice, the rate of dyeing of the colorless dye or cationic retarder is slightly higher than that of the colored dyes, but must be chosen to be of the same compatibility value. A dyebath is used containing $x\%$ modified basic dye $+ y\%$ cationic (colorless basic dye) where

"$x + y$" is equal to or slightly in excess of the fiber saturation value corrected to allow for differences in molecular weight from the theoretical 400.

Dyeing Process. Basic dyes are best dissolved by pasting with acetic acid: The acid used contributes to the bath pH of 3.6–4.0. Even where strongly anionc groups are present in the fiber, this pH is used to avoid any decomposition of dye that is possible at elevated pH and temperature. The bath will also include the leveling or retarding agent, up to 2.5-g/L sodium sulfate and, where chlorine may be present in the water supply, an antichlor such as sodium bisulfite. The temperature is brought rapidly up to just below the glass-transition temperature (80°C) and then slowly raised to 96–106°C depending on the dyes, fiber, and machinery. Temperatures >100°C are used to promote migration and diffusion after all the dye has exhausted. After an appropriate time to allow exhaustion and diffusion into the fiber, the bath is cooled to below T_g to avoid any dimensional instability.

Gel Dyeing. Continuous methods exist for dyeing wet-spun acrylic yarns while they are still in their swollen nonaligned state. The advantage of these methods is that they are extremely rapid, and the rate of uptake of dye is not dependent on glass-transition temperature so reducing the constraints on dyestuff selection.

Pad-Steam. Acrylic tow or sliver is continuously dyed by padding cationic dye and acetic acid and steaming for 5–90 min depending on depth of shade. Compatibility values are not always valid, and uniformity in fixation is difficult. The process is therefore mainly used for dyeing tow or sliver.

8. Dyeing of Polyester

8.1. Overview.

Polyester fibers are based on poly(ethylene terephthalate) (PET); some modified versions are formed by copolymerization, eg, basic dyeable polyester. The modified forms dye in analogous manner to other fibers of similar charge. Once again, the dyeing of these fibers has been discussed in fuller detail (45,46).

Unmodified polyester fibers are hydrophobic, and have a high glass transition temperature. These lead to the somewhat unusual requirements of a hydrophobic dye, and high temperature application conditions. The dyes used are disperse dyes. These have low solubility in water and and an essential part of their manufacture is grinding in the presence of a dispersing agent to create a formulation that disperses readily in water. The dyebath is a fine dispersion, and the dispersion should be stable to dyeing conditions. The dyeing process can be described by the general scheme outlined in Figure 1, in which step (a), the slow dissolution of dye from dispersed particles, is an important step. The rate of dissolution depends on the particle size of the dispersion. The mechanism of dyeing is by simple partition, the so-called solid solution mechanism. Leveling agents for disperse dyeing of polyester are nonionic surfactants that increase the solubility of dye in the bath.

At normal (i.e. 100°C or less) dyeing temperatures diffusion through the polyester fiber [Figure 1, step (d)], and thus dyeing, is very slow. The dyeing rate is increased by increasing the segmental mobility of the polymer chains of the fiber. Polyester fibers have a glass-transition temperature (or more accurately a “dyeing transition temperature”) in the region of 110°C, and thus dyeing above this temperature is much more rapid than below. Batch dyeing is usually carried out in pressurized machinery at 125–135°C. The higher temperatures also increase the solubility of the sparingly soluble dye in the dyebath and increase migration and leveling. When pressure dyeing machinery was not available, dye diffusion was usually increased by the use of a chemical “carrier” such as o-phenyl phenol, 1,2,4-trichlorobenzene or biphenyl. While they were popular, even essential, when polyester was first introduced, carriers have significant limitations. Many are environmentally questionable, they have noticeable odor, they can lead to spots and stains, they can be difficult to remove after dyeing, and they may negatively affect light fastness of some dyes. When a process still requires a carrier, newer materials with carrier-like properties are supplied as “migration accelerants” or “diffusion accelerants”. Continuous dyeing may be accomplished by the use of high temperature steam at 165–180°C, or baking (thermofixation) at 190–220°C.

8.2. Preparation for Dyeing. A hot alkaline scour with a synthetic surfactant and with 1% soda ash or caustic soda is used to remove size, lubricants, and oils. Sodium hypochlorite is sometimes included in the alkaline scouring bath when bleaching is required. After bleaching, the polyester fabric is given a bisulfite rinse and, when required, a further scouring in a formulated oxalic acid bath to remove rust stains and mill dirt which is resistant to alkaline scouring.

Other fibers blended with polyesters in numerous blended fabrics require alternative methods of preparation. Generally, the scouring and bleaching procedures used for these blends are those employed for the primary component of the blended fiber or for the component that most influences aesthetic appearance.

8.3. Disperse Dyes. There is a general correlation between heat fastness, the propensity to desorb under conditions of dry heat onto a white piece of polyester, and the dyeing properties of disperse dyes. As with other dye types, there has developed a need to subdivide them based on their dyeing behavior and fastness.

Disperse dyes were originally developed for use on cellulose acetate, and on polyester the acetate dyes have low heat fastness, tend to be small molecules, and are ideal for carrier dyeing. They also have good coverage of any physical differences in the polyester and rapid rates of diffusion and good migration. They are widely used for dyeing pale shades. Their only disadvantage is that because of their high rates of diffusion they show relatively poor wetfastness especially in staining other more rapid dyeing adjacents such as nylon and secondary acetate. They are often referred to as “low energy dyes” dyeing being effected with lower energy techniques than the other disperse dyes. Low energy dyes are not usually used in thermofixation as their low heat fastness at the thermofixation temperatures used (200–210°C) results in them subliming from the hot fabric.

Medium energy dyes are based on larger sized molecules than the low energy dyes. They have slower rates of dyeing, better heat fastness, and generally higher wetfastness. Few of them are suitable for carrier dyeing. Their main application methods are exhaust dyeing at temperatures of 125–135°C, and at this temperature their medium molecular size allows dyeing to take plce rapidly:

30 min or less. Intermediate volatility makes them suitable for continuous dyeing by thermofixation for ~30–60 s at 190–210°C.

High energy dyes are based on larger molecules with polar groups that further reduce their volatility. Thus they have excellent heat fastness resulting from extremely low rates of sublimation. Their main use is in dyeing fabrics that are to be given a subsequent high temperature heat treatment, eg, permanent pleating finish, or sewing threads whose future use and treatments are unknown.

8.4. Dyeing Processes. Polyester yarns and fabrics are usually dyed by exhaust techniques; continuous dyeing is largely confined to blends with cellulose. The dyeing process is relatively simple. The dyebath is set with disperse dye and additional dispersing agent (even though the dye as supplied contains dispersing agent). A leveling agent, usually a nonionic or anionic surface-active agent (or a blend of these) may also be added. These have the effect of increasing the solubility of dye in the bath, and thus can increase the rate of dyeing, and the leveling that takes place. A pH of 4–5.5 obtained with, eg, acetic acid or monosodium phosphate is common to avoid dye decomposition. The temperature is slowly raised up to the dyeing temperature (125–135°C) and kept there to complete exhaustion and promote migration. The rate of dyeing progressively increases as the temperature increases up to and beyond the glass-transition temperature. If dyes are used in mixture shades that are compatible throughout this heating up phase, level on-tone dyeings result. The early stages of dyeing should be slow enough to encourage level dyeing. The amount of time at the final temperature depends on the depth of shade and the energy level of the dyes used. Exhaustions of $>95\%$ are usual. Once exhaustion and diffusion are complete, the bath is cooled. Polyester fibers contain a small amount of oligomeric material, mostly cyclic trimer, that dissolves in a hot dyebath. As the bath is cooled the solubilty decreases and the oligomer can deposit on machinery and on the fiber surface. This results in the need to clean machines, or presents problems in later textile processing respectively. Dropping the dyebath as hot as possible can avoid many of these problems.

During the cooling process, the solubility of any disperse dye remaining in the dyebath decreases rapidly and it can precipitate onto the surface of the polyester fibers. If it is not removed the resulting dyeing will exhibit both poor fastness to rubbing and poor wetfastness. In any subsequent wash fastness test, these particles of disperse dye will be able to stain other hydrophobic fibers adjacent to the dyed polyester. This precipitated dye is removed by a "reduction clearing" using hot (70°C) caustic soda and sodium dithionite (hydrosulfite), optionally in the presence of a detergent. Azo dyes are destroyed, while anthraquinone dyes are solublized in the manner of a vat dye. The process does not affect dye within the fiber, indicating its unavailability $<T_g$. This process, based on strong reducing agents, can be avoided by the use of disperse dyes that are removed by aqueous alkali alone. Several means of achieving solubility by alkali treatment have been developed.

Subsequent Migration. Although it is possible to obtain excellent fastness properties by either reduction clearing of traditional dyes or alkali clearing of novel alkali-sensitive dyes, this fastness can be short lived. In any subsequent heat treatment of the polyester such as heat-setting to stabilize the fiber or fabric, the polyester is again taken above its glass-transition temperature and dyestuff molecules again have mobility within the fiber. Additionally, nonionic surfactants (leveling agents, etc.) that are insufficiently rinsed out (especially when the rinsing is carried out above the cloud point) or finishing agents such as a softener or antistat can dissolve dye from the fiber over time and make it available to stain other materials.

9. Dyeing of Cellulose Esters

9.1. Overview.

Secondary cellulose acetate was developed as a textile fiber (acetate silk) in the 1920s. Cellulose triacetate became viable in the 1950s with the economic availability of a suitable solvent (methylene chloride) from which to spin such fibers, and had somewhat polyester-like properties of heat-settability and dyeing. Triacetate is becoing obsolete, and reference to "acetate" implies the acetone-soluble secondary acetate (see FIBERS CELLULOSE ESTERS).

When originally developed, secondary cellulose acetate represented a dyeing challenge. Selected direct dyes, or temporarily soluble dyes that hydrolyzed in the dyebath were used. The technique of "dope-dyeing" (incorporating dye directly into the fiber spinning solution) was developed. Acetate fibers are now dyed almost exclusively with disperse dyes: Among the categories of disperse dyes discussed above for polyester, these are low energy dyes. Dyeing processes for triacetate tended to borrow from those being developed concurrently for polyester.

9.2. Dye Preparation.

Cellulose Diacetate. When preparing cellulose diacetate for dyeing, strong alkalies that would saponify the fiber surface must be avoided in scouring. Many fabric constructions tend to crease and therefore require open-width handling. Scouring is frequently carried out on a jig or beam using 1.0 g/L of surfactant and 0.5–1.0 g/L tetrasodium pyrophosphate for 30 min at 70–80°C.

Large quantities of acetate filament are found in satin, taffeta, and tricot fabrics; these are usually dyed open-width on a jig owing to their inclination to crease or crack easily. As with polyester, dyeing is carried out at ~pH 5, with dispersing and leveling agents. A typical dyeing procedure on the jig involves addition of acetic acid and dispersing agent over two ends at 50°C. The disperse dye is added over two ends and the dyebath temperature is gradually raised to 80°C in 5–10°C increments with two passes at each temperature. The dyeing is completed after 30–60 min at 80°C. Some dyes migrate slowly, and temperatures up to 90°C may be used.

Cellulose Triacetate. Cellulose acetate having 92% or more of the hydroxyl groups acetylated is referred to as "triacetate". This fiber is characteristically more resistant to alkali than the usual acetate and may be scoured, generally, in open width, with aqueous solutions of a synthetic surfactant and soda ash.

9.3. Dyeing Procedure.

Triacetate is a more hydrophobic fiber than secondary acetate, and dyes diffuse more slowly through it. Similarly to polyester, the rate of diffusion of the disperse dye into the fiber is increased by increasing the dyeing temperature to 110–120°C or using a dye accelerant or carrier. Trichlorobenzene, methyl salicylate, biphenyl and especially butyl benzoate are typical accelerants. Higher amounts (10–15% owf) are used for dyeing at the boil than at 110–120°C, where 2–4% carrier (or in some cases, none) suffices. Triacetate, like polyester, achieves dimensional stability by heat-setting that requires disperse dyes with good sublimation fastness.

A typical dyeing procedure for triacetate includes setting a bath containing acetic acid, dispersing agent, and carrier (amount based on dyeing temperature and liquor ratio) to pH 4.5–5.0; circulating 10 min and adding disperse dyestuffs; raising to 100°C or 110–120°C over 30–45 min; and running for 1–2 h, depending on the desired depth of shade and exact temperature. Triacetate may also be dyed continuously by the pad-dry–thermosol-scour method. The disperse dye is padded along with a suitable thickener. The goods are dried and treated in a thermosol oven for 90 s at 190–200°C, rinsed, and scoured.

10. Dyeing of Fiber Blends

10.1. Overview.

Fiber blends combine the advantageous properties of two or more fibers into one fabric. They are available as blends of natural fibers, synthetic fibers, or natural fibers blended with synthetic. The most important blend is that of polyester with cotton. The combination of the aesthetics of a natural fiber (eg, hydrophilic properties, hand) and the physical properties of the synthetic fibers (eg, strength, abrasion resistance) is an important factor in the acceptance of these fiber blends. The differences in dyeability between the many fibers on the market open a wide field of multicolored yarns and fabrics to the stylist. The multitude of fibers offered have resulted in an almost unlimited number of fiber blends in the field; usually two fibers are used together, but three-fiber blends are also relatively common. Fabrics consisting of more than one fiber type can be true (or intimate) blends in which the fibers are blended prior to spinning them into yarns. Mixed-fiber fabrics consist of single-fiber yarns that can be arranged with one fiber in the warp and another in the filling, alternate fiber yarns in each direction, or even of single-fiber single yarns plied together. Whichever way the fibers are arranged, the dyeing on each fiber can be aimed at the same shade (union dyeing), a similar shade in different depths (tone-on-tone), or a different shade (cross-dyeing). Cross-dyeing of an intimate blend does not show a shade difference between two fibers as clearly. Sometimes efforts are made to leave one fiber undyed (reserving), although a complete reserving of a fiber is not possible in all cases.

Depending on the fibers involved and the effect required, as well as the dyes used and the fastness requirements, it may be possible to dye the two fibers simultaneously in the same bath (one-bath, one-stage). The same bath may be used sequentially (one-bath, two-stage), or it may be necessary to conduct two separate processes in separate baths (two bath, two stage). For the last two, the order in which the fibers are dyed can vary. Two-bath, two-stage processes are time-consuming and inefficient of water and energy, but may be needed to achieve the shade and the required levels of fastness. Conditions can be chosen to give the maximum dyeing efficiency for each dye–fiber combination.

One-bath, one-stage processes can be useful both when the fiber blend components are being dyed by the same class of dye, eg, acid dyes on wool–nylon blends, as well as when the components are dyed by different classes that do not interact, eg, rayon–acetate blends with direct and disperse dyes, respectively. More complex situations arise when two different dye types are used that can suffer from interactions, eg, polyester–cotton blends where the alkali required for a reactive dye may cause disperse dye instability, or the clearing needed for polyester would also destroy dye on cellulose. When the fibers are dyed separately, the methods used are generally identical to those already described for the individual fibers.

A convenient means of categorizing the fibers involved in dyeing of blends is the ABCD system. 'A' represents fibers dyed with acid dyes (wool, silk, nylon), 'B' with basic dyes (acrylic), 'C' is cellulose and the dyes used for it (direct, reactive, sulfur, vat and azoic) while 'D' refers to fibers dyed with disperse dyes (polyester and acetate). Of course, some fibers may have deliberately modified dyeability, eg, basic-dyeable polyester and nylon. In addition, some fibers take up dyes that are out of their class, (eg, nylon taking up disperse and many of the cellulose dyes, wool taking up basic dyes) and anticipating and controlling the extent to which this happens is the skill of a dyer involved in dyeing such blends. As with other areas of coloration technology, the subject has been examined in some depth (54).

Pigment Coloration. The foregoing discussion assumes that the blend is being colored with dyes. The application of a pigment, in conjunction with a binder, to the surface of a fabric is superficially attractive, especially in the coloration of fiber blends, given the non-specificity of pigments for substrates. Purists do not look upon this form of coloration technically as "dyeing"; nevertheless millions of meters of fabric are colored by this system each year. A finely dispersed organic pigment is applied by padding together with organic binders and, if necessary, a catalyst. After drying, the fabric is cured at 170–175°C when film formation and cross-linking of the binder takes place. The typical binder systems used are acrylic emulsion polymers comprised of a range of monomers. No wash-off is required as all the pigment is physically bound in the resin systems. However sometimes a washing treatment is carried out to remove chemicals used in the process or to soften the hand of the fabric. Pigments include both organic and inorganic types and they give excellent lightfastness and good wash fastness in pale to medium shades. The use of pigments is most useful in pale shades, where the effect of the binder on fabric hand is less obtrusive. Pigments and binders formulated to have a cationic charge on the dispersed particles will exhaust onto the negative surface charge of fibers in water: in this way pigments can be applied by a batch exhaust process: subsequent curing of the binder is still required.

Since the pigment is held on the fiber surface any abrasion will remove color and where this happens the fabric tends to acquire a "frosty" appearance. The surface is also prone to removal by rubbing, and the crock fastness must be carefully observed and controlled by the choice of binder and the curing conditions. Fabrics most often colored this way are from light to medium weight poplins and sheetings of cellulosic or of polyester–cellulosic blends, filament polyester fabrics for draperiesand glass-fiber fabrics for bedspread, curtain, and upholstery uses. Quite often these are pastel shades with little or no afterwash required.

10.2. Cellulosic Fiber Blends.

Cellulosic–Polyester Fibers. One of the most important fiber blends on the market is the mix of cotton–polyester in roughly equal amounts, usually from 35 to 65% of one or other of the fibers.

Many apparel knitgoods consist of this fiber blend as do sheeting, shirting, and work-cloth fabrics. High wet modulus (modal) viscose fibers are sometimes used instead of cotton. Although the knitgoods are dyed in exhaust dyeing procedures, most of the woven fabrics are dyed according to one of the continuous dyeing processes. The choice of dyes and hence dyeing method is determined by the fastness properties required.

Exhaust Dyeing. The easiest way to dye cellulosic–polyester blends is a one-bath exhaust dyeing process with application of direct and disperse dyes. High temperature dyeing equipment is frequently utilized for the dyeing of cotton–polyester blends. In paler shades, where reduction clearing may not be necessary, this can be a one-stage procedure, otherwise the polyester is dyed first, cleared, and the directs applied in a second stage. A one-stage process requires a special selection of direct dyes that are stable to high temperature dyeing conditions, and which minimally stain polyester. The dyeing is conducted for 30–45 min at 125–130°C. To improve wetfastness properties, the (direct component of the) dyeings can be aftertreated. For even better fastness a combination of disperse dyes and fiber-reactive dyes are used. The classical approach is to dye the polyester first with medium or high energy disperse dyes and then clear all loose dye by reduction, before dyeing the cotton (or viscose) using the fiber-reactive dyes. In dark shades the intermediate clearing process is vital because the disperse dye also shows some affinity for the cotton during dyeing owing to the cotton being more hydrophobic than the water phase, and can give a heavy stain on this component with very low subsequent wetfastness. The disadvantage of this technique is that total processing times of 6–8 h minimum are needed.

The process time can be reduced by ~1 h by using compatible medium energy alkali clearing disperse dyes where a shorter dyeing process can be used and clearing done with alkali alone, thus reducing chemical costs. This approach gives dyeings that are equal in fastness to the classical approach.

A further refinement that has been adopted is to dye the cotton first, and after rinsing the polyester is dyed at high temperature. The polyester dyeing process acts as the washing off process for the reactive dye, but a reduction clearing at the end of the process is not feasible because the cotton is already dyed with a fiber-reactive dye that would be destroyed by the action of alkaline reducing agents. This results in a risk of lower fastness because of disperse dye precipitated during cooling, and is thus limited to paler depths of shade. Total dyeing times of ~5 h are typical.

Recently, one-bath methods have been successfully introduced based on carefully selecting fiber-reactive dyes that are stable to high temperatures and medium energy disperse dyes that are alkali clearable. The disperse dye and fiber-reactive dye are added together at the start of dyeing in the presence of dispersing agent acetic acid (pH 5.5), and sodium sulfate as electrolyte. This is used instead of sodium chloride because of that salt's corrosive attack on stainless steel machinery at high temperatures. The dyebath is raised to 130°C for ~30 min depending on shade. The disperse dye exhausts onto the polyester, and the fiber-reactive dye exhausts onto the cotton. The high temperature promotes leveling of the fiber-reactive dye. The dyebath is then cooled to 80°C and alkali added. This alkali both fixes the fiber-reactive dye and clears the alkali clearable disperse dyes. After allowing adequate time to complete the reactive dye fixation the fabric is washed as for cellulose. Total dyeing times of around 4 h are possible with excellent fastness properties. Alternatively, dyeing under alkaline conditions with stable dyes and appropriate auxiliaries has been used both for 100% polyester and for polyester cotton blends (55). Similar advantages can be obtained with reactive dyes that fix under neutral conditions (56), and using more typical disperse dyes.

Continuous Dyeing. Large quantities of cotton–polyester fabrics are dyed continuously to promote shade consistency and economy. The processes vary with the class of colorant applied to the cellulosic fiber:, sulfur, fiber-reactive, and vat dyes can be used, plus coloration with pigments is possible, depending on the fastness requirements for the finished goods. The simplest way is a pad–dry–cure process using pigments and polymeric binders for pale shades on sheeting and on shirting fabrics. For darker shades and where higher color fastness is needed, combinations of disperse/vat or sulfur and disperse/fiber-reactive dyes are applied. The most common procedures are (*1*) pad–dry–thermofix–chemical pad–steam–wash; (*2*) pad–dry–thermofix–reduction, clear–dry–pad, fiber-reactive dye–batch–wash; (*3*) pad–dry–thermofix–reduction, clear–dry–pad, fiber-reactive dye–bake–wash; and (*4*) pad–dry–bake–washoff, ie, a single-bath process.

In all methods, thermofixation conditions are 60–90 s at 190–220°C depending on the choice of disperse dye. In method (*1*), the most popular method in the United States, the chemical pad is caustic and hydrosulfite for vat dyes, and alkali and salt for fiber reactives. For sulfur dyes, the sulfur dye itself would be applied in the second pad.

Methods (*2, 3*, and *4*) are only applicable to fiber-reactive dyes. In method (*2*), the fiber-reactive dye is applied with alkali. The choice of alkali and batching times and temperature are dependent on the fiber-reactive dye used.

In method (*3*), the fiber-reactive dye is applied with alkali and urea, the choice of alkali and amounts of alkali and urea being dependent on the depth of shade. Baking conditions are ~60–90 s at 150°C. This method is popular in Asia.

Finally, in method (*4*), the fabric is padded with a mixture of medium energy disperse dyes, carefully selected higher reactivity, and rapid diffusing fiber-reactive dyes, up to 10 g/L sodium bicarbonate depending on depth of shade, and proprietary auxiliary agents.

The trend in continuous dyeing is toward shorter and shorter lengths to be processed.

Cellulosic–Acrylic Fibers. Commonly, this blend is used in knitgoods including socks and hosiery, and woven fabrics for slacks, drapery, and upholstery. Since anionic direct dyes are used for the cellulosic fiber and cationic dyes for the acrylics, a one-bath dyeing process is only suitable for light-to-medium shades. Auxiliaries are needed to prevent precipitation of any dye–dye complexes.

In two-bath processes, either the cotton or the acrylic can be dyed first. If the cotton is dyed first cationic dye can form a salt linkage with the sulfonic acid groups on the anionic dye on cotton leading to poor fastness. Heavy shades are best dyed by first dyeing the acrylic and then dyeing the cotton under neutral or slightly alkaline conditions. In order to prevent desorption of the cationic dye the dyeing temperature for the cotton dyeing must be below the glass-transition temperature for the acrylic of 80°C.

Cotton–acrylic fiber blends are also used for high quality upholstery pile fabrics. Besides the one-bath exhaust dyeing procedure involving a very high ratio of liquor to fabric, a continuous pad–steam process is used to dye these fabrics. After padding, the goods are steamed for 7–15 min at 98–100°C. The material then must be rinsed warm and cold before drying.

Cellulosic Fiber–Nylon Blends. These blends are used in fabrics for apparel, corduroy, socks, and swimwear. If wetfastness requirements are relatively low, the nylon portion can be dyed with disperse dyes and the cellulosic fiber with direct dyes and a one-bath procedure can be employed. For better wetfastness, the nylon portion is dyed with level dyeing acid colors together with the direct dyes in one bath at 95°C using a reserving agent (typically a phenolsulfonic acid condensation product) to prevent the direct dyes from dyeing the nylon. An aftertreatment with a cationic fixative improves the wetfastness properties of the direct portion of the dyeing. For swimwear, the cotton portion is dyed with fiber-reactive dyes: These will tend to dye the nylon, either in reactive or hydrolyzed form. Careful dye selection, the use of a resist agent, and soaping under slightly alkaline conditions can minimize this. After rinsing hot and cold and soaping at the boil, selected acid and/or acid milling colors are applied to the nylon portion with a phosphate buffer system. An aftertreatment with a syntan results in best wetfastness properties.

10.3. Wool Blends. *Wool–Cellulosic Fibers.* One of the oldest fiber blends in the textile market is the combination of wool and cotton or wool and viscose. Economy was the primary reason for this blend. Selected direct dyes, which dyed both fibers from a neutral bath in a uniform shade, or a combination of neutral-dyeing acid dyes with direct dyes, were used to dye this fiber blend. However, problems with cross-staining, shade reproducibility, and loss of strength of the wool fiber by boiling in a neutral dyebath (pH 6.5–7.0) led to development of the one-bath process. Selected direct and acid dyes are applied at pH 4.5–5.0 at 98–100°C. A reserving agent is used (as in cellulose–nylon blends), to prevent the direct dyes from dyeing the wool under acid conditions. If optimum wetfastness properties are required, fiber-reactive dyes can be applied to both fibers by use of a two-bath process.

Wool–Nylon. Nylon has been blended with wool in order to give additional strength to the yarn or fabric. It is used mainly in the woollen industry for coats and jackets and, to a lesser extent, for socks and carpet yarns. Both fibers are dyed with the same products, however, the fibers have different affinity to them. Generally, level dyeing acid dyes are applied. Disulfonic acid types are preferred for light to medium shades because they dye both fibers more easily in the same depth as monosulfonic acid types. However, in most instances a reserving agent is needed for light to medium shades to balance the depth between nylon and wool. Without it, the nylon dyes more strongly.

For heavy shades, monosulfonic acid types are preferred to obtain the necessary buildup on the nylon. In case the nylon remains lighter than the wool, a small amount of disperse dye is added to the dyebath to build up the depth on this fiber.

Wool–nylon upholstery fabrics and carpet yarns require higher light- and wetfastness properties. Neutral premetallized dyes are used in these cases. However, they have a much higher affinity to the nylon than the wool. Therefore, stronger retarding agents have to be employed, eg, phenolsulfonic acid condensation products. Higher amounts are required for light shades than for medium depth. Dark shades can be dyed without addition of a retarding agent.

Wool–Acrylic Fibers. This blend is being used for industrial and hand knitting yarns. The acrylic fiber is aesthetically similar to wool, increases the strength of the yarn, and adds bulk to the goods. Special precautions are necessary since the two fibers are colored with dyes of opposite ionic type. Coprecipitation is prevented with the use of an antiprecipitant. Usually, level dyeing acid dyes are used for the wool portion in combination with the cationic dyes for acrylic fiber.

Wool–Polyester Fibers. The 45–55 wool–polyester blend is the most common fiber combination in the worsted industry. Strength and excellent dimensional stability of the polyester fiber enable the creation of lightweight wear fabrics not obtainable before. Economy has modified the fiber ratio and 30–70 and 20–80 wool–polyester blends are as common as the classical 45–55 blend. Disperse dyes for polyester and acid or neutral premetallized dyes for wool are employed in a one-bath process. Normally, wool blends should not be dyed >105°C in order to avoid deterioration of the fiber quality, and the dyeing of the polyester portion of this blend in exhaust dyeing processes would use a carrier. However, wool protective agents have been developed that allow wool to survive dyeing processes of up to 120°C for limited periods, and that permit carrier-free dyeing leading to higher fastness (57).

10.4. Blends of Synthetic Fibers. *Polyester Fiber Blends.* Disperse dyeable and cationic dyeable polyester fibers are frequently combined in apparel fabrics for styling purposes. Whereas the disperse dyes dye both fibers, but in different depths, selected cationic dyes reserve the disperse dyeable fiber completely, resulting in color/white effects.

Polyester Fiber–Nylon Blends. This fiber blend is used in apparel fabrics as well as in carpets. Disperse dyes dye both fibers, however they possess only marginal fastness properties on nylon. Therefore it is important to select those disperse dyes that dye nylon least under the given circumstances. The nylon is dyed with acid dyes, selected according to the fastness requirements. The fiber blend is dyed in a one-bath process for 1 hour at 100°C or at 115–120°C. Cationic dyeable polyester–nylon blends and blends of nylon with both polyester types are also in use. The three-fiber blend is dyed according to a one-bath two-step process. The disperse dyeable portion and nylon are dyed first in one bath, followed by the cationic dyeable polyester.

Polyester Fiber–Acrylic Fiber Blends. This fiber blend is dyed in a similar fashion to that of the blends of the different polyester fibers. The selection of cationic dyes is substantially larger for the acrylic blend. There is concern about the disperse component dyeing the acrylic fiber and leading to reduced fastness of the blend, and the use of temperatures above 110°C to which acrylic fibers are sensitive limits the choice of disperse dyes and thus the ultimate fastness properties

Nylon Blends. Differential dyeing nylon types and cationic dyeable nylon blends are used primarily in the carpet industry. The selection of cationic dyes for nylon is rather limited; most products have very poor fastness to light. These blends are dyed in a one-bath procedure at 95–100°C. Selected acid dyes are used for differential dyeing. Disperse dyes will dye all different types in the same depth.

Elastomeric Fibers. Elastomeric (spandex, elastane) fibers are mostly polyurethanes. They are combined with nonelastic fibers to produce fabrics with controlled elasticity (see FIBERS, ELASTOMERIC). Processing chemicals and conditions must be carefully selected to protect all fibers present in the blend. Prior to scouring, the fabrics are normally steamed and/or heat-set to relax uneven tensions placed on the fibers during weaving or knitting. Scouring, which is used to remove lubricants and sizing plus oils that derive from the polyurethane fiber, is normally conducted with aqueous solutions of synthetic detergents and tetrasodium pyrophosphate: the use of solvents and solvent emulsions has declined in recent years.

When bleaching is required, a reductive bleach with sodium hydrosulfite and sodium metabisulfite is used. Cotton blends may require a hydrogen peroxide bleach at pH 9.0–9.5 prior to or instead of the normal reductive bleach. Chlorine-type bleaches which damage elastomeric fibers are avoided.

Polyurethanes are dyeable with many acid dyes and disperse dyes, and in blends with nylon both components are colored by the acid dyes used. The fastness on the polyurethane is less than on nylon, thus the selction of dyes to minimize cross-staining is critical in obtaining satisfactory fastness. Post-dyeing application of fixatives is helpful. Blends with polyester would be economically advantageous, but the high temperature required for efficient dyeing of polyester is damaging to spandex, and the disperse dye stain on spandex limits wet-fastness, although thorough clearing can go some way to answering this problem.

10.5. Speciality Uses. In addition to polyester–cellulosic and cellulosic fabrics, pigments may also be applied to 100% synthetic fibers of special construction for unique uses. Examples are 100% filament polyester for draperies and glass fabrics for bedspread, curtain, and upholstery uses. This type of fabric is usually run on a finishing frame by going through the padder, with drying and curing in the tenter housing. Quite often these are pastel shades with little or no afterwash required.

10.6. Solvent Dyeing. Solvent dyeing generally refers to dyeing in nonaqueous media. In the energy-conscious early 1970s, the lower amounts of energy required to heat organic solvents to dyeing temperatures, was expected to make solvent dyeing technically important and the techology was discussed and researched extensively (58,59). This interest did not materialize into practical acceptance, chiefly on cost and environmental grounds, and the technique has not achieved importance.

11. Dyeing Machinery

The general subject of machinery for dyeing textiles from an engineering perspective has been discussed in detail (60).

11.1. Batch Dyeing.

In the batch exhaust application of dyes, agitation is essential to ensure a level result. The dye liquor and the substrate must be moved relative to each other, and this may obviously be accomplished by moving the bath, the material, or both. All three possibilities are used in practice.

Overview. Certain aspects of batch dyeing equipment are common to whatever type of material is being processed. Stainless steel is the universal material of choice for dyeing machinery. It is minimally stained by dyes, and resists corrosion by most of the conditions used in dyeing processes. The use of chlorite, or of chloride ions at temperatures above the boil, can cause corrosion. Heat is supplied to dyeing machines in the form of steam: a boiler is an essential item of equipment in a dyehouse. Formerly, "live" steam would be injected directly into the bath. While this transfers heat efficiently, and provides agitation, the condensed steam alters the liquor ratio and any impurities in the steam enter the dyebath. Cooling in such a machine is slow, or is accomplished by the gradual replacement of dyebath with cold water. Modern machines are equipped with heat exchangers: These are essential for pressurized machines. The same exchangers can also provide cooling, which cools more quickly and maintains the bath conditions accurately if any additional processing is required.

Over the years, the dyer and machinery manufacturer have applied mechanical and electrical equipment to improve the control and repeatability of dyeings. The major control is that of temperature: the installation of thermometers was followed by remote recording, and later by preprogrammed heating and cooling cycles, first by mechanical and now by electronic means. Systems for similarly controlling pH have been developed but have been far less widely adopted. Pressures, water volume, flow rates, and fabric speed and tension can all be measured and controlled.

Control can extend outside the dyeing machine and there are many examples of completely automated computer-controlled exhaust dyehouses that control loading, unloading and drying of the material being dyed. They also provide management with tools to determine real time cost and energy–utility consumption. Such processes rely on highly repeatable no-add dyeing methods, which are not always assured.

In most situations, no-add dyeing is not (always) practicable, and the shade of the dyeing must be checked before the process is ended and the material removed. Machines are thus designed with some facility for sampling the dyeing. It is not always easy to provide an easily retrievable sample that has undergone the same conditions as the bulk of the material, and levelness cannot be checked this way.

Dyeing Fiber and Tow. Fiber and tow coloration have been described in practical detail (61). Fiber dyeing is usually accomplished by pumping dye liquor through a stationary mass of fibers. Fiber is prepacked into some form of perforated basket, which is then loaded into the kettle or kier containing the dyebath. Packing must be even to avoid the creation of channels and tight spots and consequently unlevel dyeing, although since the fiber is later to be thoroughly mixed in yarn formation, unlevelness is more tolerable in fiber dyeing than in yarn or fabric dyeing. During dyeing the kettle is usually enclosed, and many fiber dyeing machines are capable of dyeing under pressure at temperatures $>100^\circ$C. For efficiency of machine use, several fiber baskets per machine are used so that unloading and loading of fiber can be accomplished at the same time as dyeing is taking place.

Sliver and top are loose, untwisted ropes of staple fibers: tow is the equivalent version of filament fibers. These are often dyed in continuous form, but batch methods are available, particularly for top. Once again the material is packed in a perforated container, (a "can") that is placed in a kettle and through which the dyebath is pumped. Several arrangements are possible, including those that involve one large can in the kettle, and others than pack fewer tops into several smaller cans: In the latter case the dye is pumped through each can via a perforated spindle.

Dyeing Yarn. Yarn is dyed in one of two forms: skein or package. While obsolete methods of skein dyeing involved moving skeins through a stationary bath, in both cases today the dyebath is moved through yarn that is held in place. Skeins (or hanks) are hung from poles: The use of two poles per skein keeps the skein extended during dyeing. A frame with many poles is suspended in the dyebath, and the liquor is circulated (usually upward to float the skeins off the poles and avoid "stick marks") through the mass of yarn. Since the yarn is only partly constrained the method allows the yarn to achive bulkiness, and the method is useful for knitting and carpet yarns. The lack of firm constraint and the risk of tangling prevents the use of high liquor flows, so dyeing methods have to be adjusted to provide slow exhaustion to get levelness, and the machines tend to involve the use of high (20–30:1) liquor ratios. Skein dyeing involves winding the skeins from cones, and backwinding onto cones after dyeing. Together with the loading and unloading onto the poles, the overall process tends to be labor intensive. Few, if any skein dyeing machines are pressurized for dyeing at elevated temperatures.

In package dyeing, yarn is wound onto perforated metal or plastic formers in the form of conical or parallel sided cylinders, called cones or cheeses respectively. In some cases, the yarn spinner can supply packages that can be dyed without rewinding, but whoever does the winding, it must allow for the even passage of dye, and for any shrinkage or relaxation of the yarn under dyeing conditions. Several packages are placed on perforated spindles of a carrier: depending on the diameter of the packages, different carriers might be used in a given kettle. Horizontal spindle machines including those consisting of multiple single-spindle kettles have been developed, but usually multiple spindle carriers arranged vertically are used. Cones use spacers to hold the packages apart: For cheeses the formers are flexible and the packages are compressed together on the spindle to form one solid mass of yarn. The whole carrier, with many spindles carrying packages, is placed in the kettle where dye liquor is pumped through the spindles and through the yarn. Generally, the flow is from inside to outside of the package, but periodic reversal increases levelness. High circulation (30 liters per $\mathrm{kg}^{-1}\ \mathrm{min}^{-1}$, eg) allows for more rapid dye cycles and low liquor ratios (10:1 or so) make these machines efficient of time, chemicals and energy. Careful winding can allow for the development of some bulk in the yarn, but generally package dyeing provides "leaner" yarns for weaving. Most package dyeing machines are capable of dyeing under pressure at elevated temperatures.

Skeins and packages are bulky forms of textile materials and drying them can be slow. Mechanical removal of water by hydroextraction or (for packages) by blowing cold air is carried out first. Final drying is either by blowing warm air through a package, or suspending the skein or package in an oven: drying may take several hours. In many modern operations the quicker and more efficient radio frequency drying is carried out.

Dyeing Fabric. Probably the majority of textile material is dyed in the form of fabric. Four different machine types have been developed for the batch dyeing of such “piece goods”.

Beam Dyeing. This method is akin to package dyeing of yarn: Flat fabric is wound onto a perforated steel cylinder placed in a kettle through dye liquor is pumped. This machine is therefore akin to the fiber and yarn machines discussed so far in that the material remains stationary while the dyebath moves. Careful winding is essential to provide even liquor flow and thus level dyeing. Pressurized and unpressurized versions have been produced, and the method is good for lightweight synthetic-fiber fabrics through which liquid flows easily. Since the fabric is constrained and flat, it is also useful for materials that might crease.

Jig Dyeing. Fabric is also dyed in flat form in a jig dyeing machine (or jigger). However, in this machine the liquor is stationary while the fabric is run through it. Several hundred meters of cloth are wound around a roller on one side of a jig. The goods are run off the beam through a small-volume (400 L), V-shaped dyebath and wound on to a second beam opposite. There are friction brakes on each beam that control tension. When the entire cloth has been wound on the opposite beam, the clutch is reversed and the cloth travels back in the opposite direction. The running of the cloth from one beam to another is called an “end”. Dyeing procedures for a jig are generally run for a certain number of ends rather than for certain times. The fabric is in contact with the dyebath for the very short time that it passes through the bath: The diffusion processes occur as the fabric is turning on the beam. Because contact with the dye liquor is for such a brief time, the cloth temperature is somewhat (say 2–5°C) lower than that of the dyebath. The liquor ratio in a jig machine may be as low as 2:1, and the process thus benefits dyeing procedures that are liquor ratio dependent. The sub-100°C temperatures and low liquor ratios make the jig especially suitable for cotton fabrics: The flat form is also helpful in avoiding creases in filament acetate and nylon fabrics. It is less useful for materials that are damaged by tension and that need higher (>80°C) temperatures although enclosed and pressurized jigs have been produced. The bath is shaped so that a much higher volume of liquid can be used in rinsing steps.

The two ends of the fabric experience different dyebath concentrations as dye is preferentially taken up by the fabric, and conditions must be controlled to minimize the resulting shade change along the fabric, called “ending” or “tailing”. The sides of the fabric are more exposed to the atmosphere and cool quicker: This too can result in shade differences across the fabric (listing). The low liquor ratio and rapid speed of fabric through the dyebath, plus the centipetal force developed on the beam, make the reproduction of jig dyeing on a lab scale especially difficult.

Many improvements have been made to streamline performance and to reduce machine operation labor. Some of these are tensionless jigs using variable speed electric motors with built-in drag for brakes, automatic reversing equipment, and automatic temperature and level controls. Vacuum slots and water jets can assist in the interchange of liquid in rinsing.

Winch or Beck Dyeing. This is one of the oldest mechanized forms of dyeing fabric. Like the jig, the bath is stationary while the fabric moves to provide the relative motion. Machines can run fabrics in either open-width or rope forms. Open-width machines are reserved for heavyweight material, such as carpets, and the beck is usually considered a rope-form machine. The machine in its basic form consists of a shallow box (the beck) which has a gradual low curvature in the back and a rather high vertical rise in the front. A false front shields a reservoir into which dyes and chemicals can be added, and in which the heating coil or live steam heats the bath. About 2 m above the top of the U-shaped box is a driven elliptical reel (the winch). Fabric pieces are provided in lengths of ∼100 m. One end is passed over the top of this reel and sewn to the back end to form an endless loop. Machines can accommodate multiple ropes (usually 6–24) that run side by side. A long bar running over the length of the tub has pegs every 25–30 cm that keep strands separate and prevent them from tangling. Machines have been developed that allow the strands to be threaded as one long spiral rope which runs as a continuous belt. The tub is filled with the dye liquor and the fabric is immersed in it. The turning elliptical reel lifts fabric from the front of the dyebath, over the top of the reel, and redeposits it at the back of the bath. The fabric then slowly moves forward through the dye liquor from the back of the winch, where it is again lifted by the reel.

Becks and winches are generally enclosed machines, and run at comparatively high liquor ratios. Together, these allow for dyeing processes at the boil, although the provision of heat at the front of the machine means that a temperature difference from front to back is common. The rope form, and the gentle action make it suitable for delicate fabrics. The beck machine is thus the traditional machine for dyeing wool fabrics where temperatures at or near the boil are used, and in which high exhaustions can be obtained at long liquor ratios (cf the jig for cotton). However, it lends itself to many other types of fabric. The development of pressurized versions of the beck machine was largely preempted by the development of the jet dyeing machine.

Jet dyeing. Jet dyeing machines have become the most popular batch dyeing machine: most new machines installed are of this type. Like the beck machine, fabrics are processed as end-joined loops in rope form. In its original and most basic form, the jet machine replaces the winch as the means of moving the fabric with a narrow orifice into which dye liquor is pumped. This forms a venturi and drives the fabric at speeds of 200 m/min or more. Each fabric rope needs its own jet. The very high fabric/liquor interchange provides good penetration of substrates and makes rapid dye cycles, using high rates of heating and cooling, possible without risking unlevelness. Together with the low liquor ratio, high interchange leads to a constant temperature throughout the machine again promoting levelness. The fabric is also under less tension, and thus is less distorted and more able to bulk up. A liquor ratio of 1:10 or lower is usual, as compared to 1:20 for the beck. Jet machines are almost invariably capable of working under pressure at elevated temperatures Although the capital cost of jet machines is higher than winches, the efficiencies of water, energy, chemicals and time more than compensate.

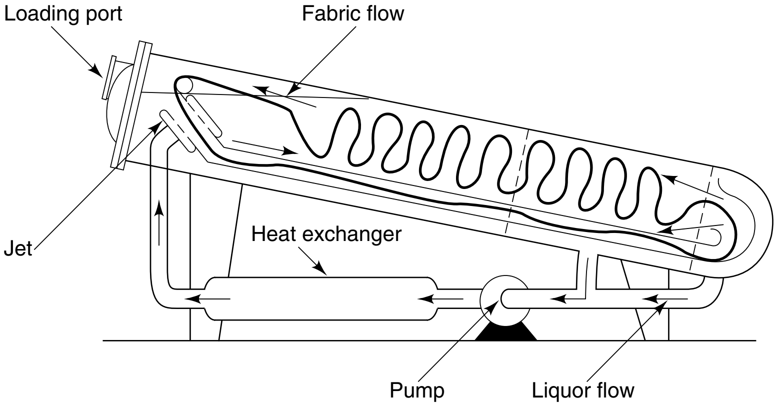

Fig. 10. Long cylindrical jet dyeing machine. The fabric return and jet are shown inside the main tube. In some designs it could be external to the main tube.

While becks and jigs tend each to have a fairly uniform layout, jet dyeing machines come in a variety of styles although two main types exist: the long horizontal cylindrical machines (Fig. 10) ideally suited for synthetic fabrics where the fabric travels along the length of the cylinder, or (Fig. 11) cylindrical or upright pear or bell-shaped, or J-box autoclaves where the fabric moves around the circumference of the cylinder or equivalent shape. These autoclave types can have more than one fabric rope per autoclave and are suitable for most fabrics.

The disadvantages of these unmodified jet machines derive from the high levels of agitation. Delicate fabrics can be distorted or damaged (in the case of

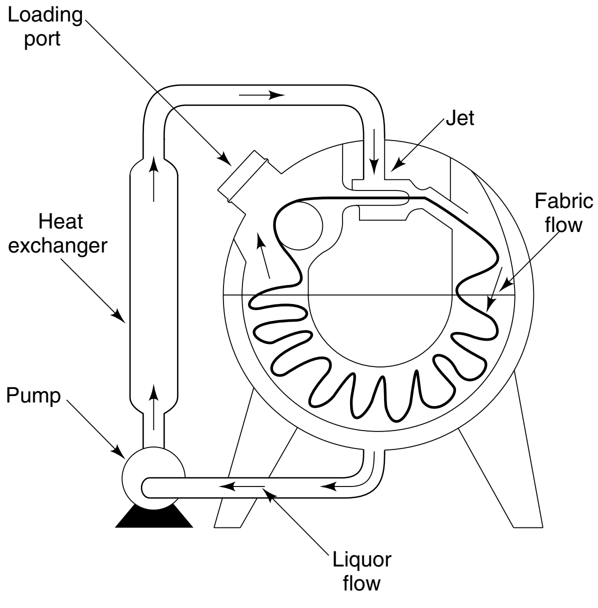

Fig. 11. Upright cylindrical jet dyeing machine.

wool, felted). Since many of the dyebath auxiliaries employed are surface active agents, excessive foaming makes the use of antifoam chemicals commonplace. These bring with them an added complexity to the system that can lead to unlevelness.

Since the introduction of the first jet dyeing machines, several developments have been introduced. They tend to involve two approaches that run in different directions: gentler action that preserves the surface appearance and stitch definition when processing delicate fabrics, and increased efficiency in energy, water and chemical use from lower liquor ratios.

Gentler action has been sought in a number of ways. “Overflow” machines (Fig. 12) also feature a driven reel that provides motive power to the fabric, plus some driving force on the cloth from the circulation of the liquor through the overflow tube down which they both pass.

Dyeing Garments. A market segment for dyeing finished articles has existed for a long time, and several types of garment dyeing machines were developed many years ago. The management philosophies of “quick-response” and” just-in-time”, coupled with the relaxed and distressed garment looks that have been fashionable, brought garment dyeing back into focus, and a new generation of machines were developed in the 1980s and 1990s. Garments do not lend themselves to close and orderly packing in a dyeing process (compared, say, to yarn in package form) and, consequently, liquor ratios must be higher. Garments must be constructed with dyeing in mind, and the materials used for sewing thread, zipper facings, buttons and other trim should be chosen carefully. Allowance should be made in sizing for any shrinkage that takes place. Garment dyeing postpones the color decision to the last possible minute, and in theory, it is possible to place several color choices on the market in limited quantities and replace the better selling items rapidly in the stores, reducing the numbers of unsold goods at the end of a season.

Among the older machines are paddle machines in which a bath is circulated by a paddle. The bath may be an annular oval, with the axle holding the

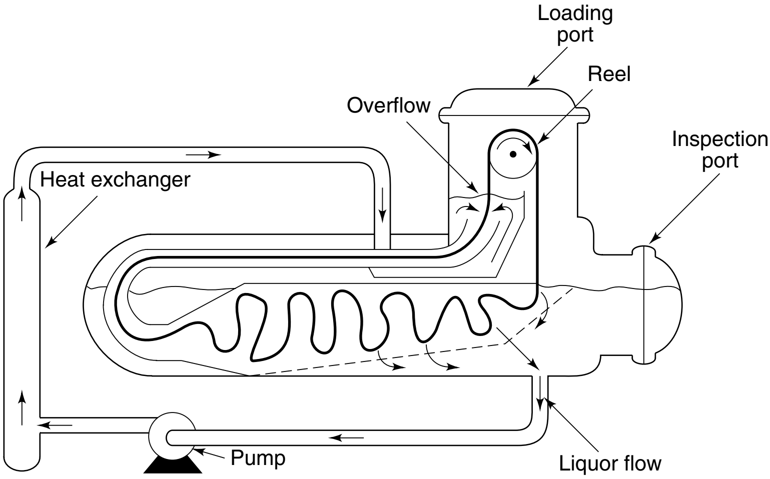

Fig. 12. Pressurized overflow jet dyeing machine.

paddle blades just above the liquor surface. As the paddle rotates it moves liquor and goods around the annulus. Alternatively a v-shaped bath is used in which the paddle forces liquor and goods downward. For hosiery dyeing, a widely used machine used a perforated drum, divided into compartments, rotating in the dyebath.

Newer machines tend to be based on front-loading commercial washers/drycleaning machines. Again, a rotating perforated compartmentalized drum revolves in the dyebath, although the design allows for low liquor ratios as the garments are not continuously submerged. These newer machines also include hydroextraction cycles.

11.2. Continuous and Semicontinuous Dyeing.

Continuous dyeing separates the individual steps of a batch process (application, fixation/diffusion, rinsing, etc) into different machine elements of a dyeing range. As the name implies, uncolored material and dye are fed in, and colored material emerges, continuously (62). The multiplicity of components in the range means that at the end of dyeing one color, several different pieces of machinery must be cleaned before a new color can be dyed. The individual components can also be controlled separately, and bringing them all into adjustment can take time during which some material is produced off-shade. Continuous dyeing is thus used in those cases where a large volume of the same color is to be dyed, and in those cases, it is an efficient process. Recent trends have tended to reduce the yardage per shade, and thus the importance of continuous dyeing, although improved controls designed to facilitate rapid changeover of shades have been introduced. For example, when the line stops, instead of switching off infrared heaters, baffles are brought between the cloth and heater or the heater is revolved to point away from the cloth to both avoid any risk of scorching the fabric or having to heat up the dryer again when starting the next shade. Quick changing pad systems have also been developed.

Continuous dyeing can be applied to fiber, yarn, and fabric. Material such as loose fiber that is not self-supporting requires some supporting conveyor system to carry it through the steps of the process. This is a complication, and although successful fiber, top, tow and yarn dyeing ranges are in use, continuous dyeing is most suited to fabric, and most woven goods, other than stretch fabrics, can be continuously dyed. Continuous yarn dyeing is most commonly used in the application of indigo to warp yarns to be woven into denim.

The different fibers, dyes and processes for applying them is reflected in the variety of equipment that is used in continuous dyeing. Application of dye may be followed by intermediate drying, and the application of other chemicals. Fixation may be accomplished in seconds, or require a longer dwell time, in dry heat, or in steam from which air may have to be excluded. Washing off may be a simple or more involved process.

Dye application may be via a spray, or by foam, but is most often done by padding, in which the material is immersed in dye solution, then squeezed between rollers to reduce and control the uptake to a consistent level (dip and nip). The cloth is passed through a stainless steel pad box, down under a rod or a roller that is below the dye liquor level. The feed of dye solution must be controlled to maintain a constant volume in the trough. Lower volumes reduce the waste at the end of a run, and also the extent to which dye substantivity will change the shade as the first meters of fabric are processed: typically the volume of the trough is completely replaced in <5 min. Conditions are adjusted to minimize the substantivity: This may mean a heated solution, but temperature variation can cause changes in shade along the fabric. The mathematical treatment of these variables and the prediction that ending is complete once the trough volume has been replaced 2–3 times was established a number of years ago in some elegant work (63,64). Some means of agitation may be included in the trough to ensure consistent solution across the fabric. The dwell time in the solution is very short, and fabric must be well enough prepared to allow for rapid wetting. In addition, padding solutions typically include a wetting agent. Some systems use two dips and two nips to achieve more thorough wetting.

The expression of excess dye is accomplished by squeeze rollers, referrred to as bowls. Most bowls consist of a medium density rubber roller across the width of which pressure can be applied. This roller presses against a stainless steel or a hard rubber roller. These rollers may be mounted either vertically or horizontally (Fig. 13) between the squeeze rollers.

Wet add-on varies between 35 and 80%, depending on the material and the force applied to the bowls. The tightness of the squeeze is controlled by weight levers, hydraulic pressure, or compressed air. Modern padders are available that allow for different pressures to be introduced across the width of the squeeze roller in order to equalize any variances in fabric adsorption across the piece, and to accommodate wear/distortion over time.

Drying prior to fixation (predrying), is used to reduce the moisture content below that where migration can occur. Intermediate drying can also be needed between the two pads of a two-pad system: padding "wet on wet" is less reliable

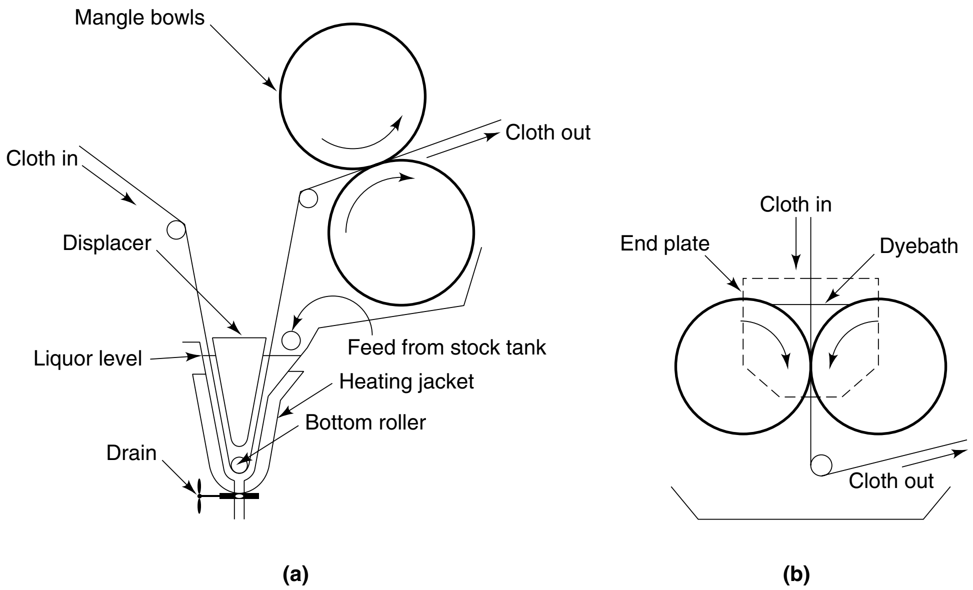

Fig. 13. Typical pad mangle configuration: (**a**), inclined vertical pad mangle with V-shaped trough; (**b**), horizontal wedge-nip pad mangle.

in controlling the uptake from the second pad. If it is necessary, such drying may be via infrared heating (ir), or a hot air continuous oven. Whichever is used, care must be taken that the movement of water to the evaporating surface is not accompanied by movement of dye, and even treatment of both sides of the fabric is essential. Antimigrants (usually water-soluble polymers that increase solution viscosity) are often included in the pad-trough formulation.

In batch dyeing, “fixation “ is reserved for reactive dyes, and is separated from the exhaustion that is common to all dyes: in continuous dyeing, exhaustion is less apparent, and the term fixation is used to cover both the diffusion into the fiber of padded dye and the reaction of reactive dye. Fixation may be accomplished simply by batching: dividing the continuously padded material into shorter lengths and rolling them up, and allowing fixation to take place while standing, usually at ambient temperature.

Fully continuous dyeing requires continuous fixation. This may simply be via heated air which is common for the thermosol dyeing of disperse dyes, the curing of binders in pigment/binder coloration, and can also be used for fixing reactive dyes on cellulose. Most often it is accomplished with saturated steam that provides the moisture required to dissolve the dye, swell a hydrophilic fiber, and allow diffusion. Air-(ie, oxygen-)free steam is essential in the fixation of vat and sulfur dyes if premature oxidation is to be avoided. In all fixation, levelness can depend on fabric tension, and the even application of fixation conditions from side to side and back to front of the fabric. In a steamer, it is important to avoid condensed water droplets.

In the continuous dyeing of blend fabrics dyes must be fixed on both fibers. For polyester/cotton blends, this usually means two fixation steps with chemical application in between, even if the dyes are applied in a single pad.

After fixation, the fabric must be rinsed. Rinsing can vary in severity depending on the dye-fiber system in use. Rinsing is accomplished in a series (up to 10 or so) of wash boxes, hot or cold, with or without a surfactant. Where several boxes have the same composition, a counter current flow between them is usual. Fabric is finally dried, in a tenter frame, or over heated cylinders.

12. Textile Printing

12.1. Overview.

Printing produces colored designs or patterns on textile substrates through a combination of various mechanical and chemical means (65). Textile materials can be printed at different steps of the textile manufacturing process: printing can be done on yarns in skein form, on warps being passed from a warp beam to another beam. Space printing is a process where a yarn, temporarily knitted into a loose fabric, is printed and then deknitted. Carpets can be printed in woven or tufted constructions. Vigoureux printing is the printing of woolen slubbing. However, printing is largely confined to fabrics: woven fabrics comprise the largest percentage of printed goods, and in recent years, knitted textile fabrics have considerably increased in importance.

In printing on textiles, a localized dyeing process takes place, in which the usual chemical and physical interactions of dyeing apply. The major differences lie in the need to provide a clearly defined design, often with sharp edges, and at the same time achieve levelness within areas of color. While there are several significant variations and alternatives discussed later, printing, like continuous dyeing, generally consists of application, fixation, and washing off steps.

Most paper printing is carried out using the four process colors, yellow, magenta, cyan and black. Different colors arise by the mixing of these four colors on the substrate. In comparison, most textile printing does not allow for reliable mixing on the substrate, and each color in the design must be separately premixed and applied: in paper printing these would be referred to as "spot colors". Designs typically contain from 1–12 colors, although higher number color prints are possible. Taking a design on paper or in an electronic file, and separating the colors prior to printing is an important part of the process.

The colorant (dye or pigment) is applied as a dispersion or solution from a vehicle called print paste or printing ink. The paste must have the appropriate flow properties (rheology) to give good transfer from the print machine onto the fabric, good levelness in large printed areas, but a sharp mark for the details of the design. It should also hold the colorant in place until fixation occurs. For dye prints, the thickener should be readily removed after printing. For pigment prints the thickener, which remains on the substrate, must be unobtrusive, requiring a material that thickens at low solids content. The required shear-thinning viscosity characteristics are achieved with hydrophilic polymers: while there is a long history of thickening agents that have been used, the most commonly used today would be natural sodium alginate, or synthetic polyacrylic acid derivatives. The technically satisfactory oil-in-water emulsions have been largely abandoned for environmental reasons.

The print paste contains, in addition to the colorant, whatever other chemicals are required for satisfactory application. These can include solvents or other materials that enhance dye solubility, actual or potential pH modifiers, and humectants that encourage the sorption of water during steaming.

After application and any intermediate drying comes the fixation process. The printed textile material is exposed to heat, heat and steam, or chemical solutions to allow fixation to take place: Obviously this can vary widely with the colorants and fibers being used. During this treatment, the dyes diffuse from the fiber surface into the fiber structure and undergo physical or chemical bonding to the fiber. In case of pigment prints, binders applied simultaneously with the pigment form films during a heat treatment and give the print the final desired fastness.

In contrast to pigment prints, dye prints must be afterscoured. In this step, the prints are rinsed in a detergent solution to remove auxiliary chemicals, thickening agents, and portions of unfixed dyes remaining on the surface of the printed fibers. Frequently, the scouring operation includes the use of chemicals assisting in removal of dye or preventing redeposition (backstaining) of dye on the white or paler areas of the print. The use of steam in fixation, plus the necessary washing off steps has led to the term "wet-printing" to refer to prints using dyes.

12.2. Colorants for Textile Printing.

Pigments. Pigment-printed textiles represent the highest percentage of all printed textiles, accounting for between 40 and 50% of all cellulose and >90% of polyester–cotton blend prints. This is primarily the result of the uncomplicated process, low cost of imparting colored patterns to textiles with pigment systems, and their applicability to all fibers.

Pigments have no affinity for textile fibers: Coloration is achieved by bonding the pigment to the fiber surface with a binder material. These are almost exclusively acrylic emulsion polymers the monomer content of which can be changed to control various aspectsof the final print: hand, fastness to crocking, etc (62). Pigment print systems have a number of inherent limitations. The binding agent and cross-linking chemical camouflage fiber texture and luster, and negatively affect the hand and feel of the textile material. While the fastenss to light of pigments is generally better than that of dyes, pigment prints can have insufficient fastness to crocking, abrasion, washing, and drycleaning, noticed especially in heavier shades and on large coverage. Abrasion of the textile leaves a frosted surface appearance that is sometimes objectionable. Set against the limitations are the undoubted economies that come with the simple application (print/dry/cure) and applicability to all substrates with little change in formulation.

Disperse Dyes. Disperse dyes are used in powder or paste form, or ready-to-prepare aqueous dispersions for incorporation into a thickener solution. For disperse dyes that show sensitivity to alkaline hydrolysis or reduction during fixation, an acid donor or acid, and, if necessary, a mild oxidizing agent, are added to the print paste.

On polyester, the fixation conditions are more rigorous than on other disperse dyeable fibers, owing to the slower diffusion of disperse dyes in the fiber. For continuous fixation the prints are exposed to superheated steam under pressure at 170–180°C for 6–8 min. A carrier is essential if lower temperature unpressurized steam is used. Dry-heat fixation conditions of 170–215°C for 1–8 min tend to affect the fabric hand and are less popular for printed fabrics, but are sometimes employed because of lack of other equipment: medium to high energy disperse dyes should be used to avoid dye sublimation causing staining of pale or unprinted areas, or a loss of definition of the printed mark.

For short runs, batch-type fixation can be used via a pressurized autoclave with saturated or nearly saturated steam at 14–18 kPa (105–135 mm Hg) and 125–130°C for 45–60 min.

Afterscouring of polyester prints generally includes a reduction clearing with sodium hydrosulfite and alkali at 60–80°C to remove any dye remaining on the fiber surface.

On polyamide, disperse dyes have generally low wetfastness properties, making them unsuitable for printed textiles that require even moderate wash or perspiration fastness.

Acid and Premetallized Dyes. Comparatively little wool is printed, and acid dyes are most widely used in printing polyamide: woven or knitted fabrics for apparel, swimwear, drapery, and upholstery materials. Dyes are usually of the higher fastness types: acid leveling dyes are rarely used in printing. The dyes are dissolved in hot water, which can, depending on the solubility of a specific dye, include a dye–solvent such as thiodiethylene glycol or diethylene monobutyl ether. Acid dyes supplied in liquid form can be added directly to the thickener solution. In case of the print–dry-steam operation, 3–5% of urea or thiourea is also added to the dye solution to act as humectant during fixation.

The print paste contains an acid donor, usually 1–3% ammonium sulfate, and in some cases a small amount of oxidizing agent such as sodium chlorate to prevent reduction of the dye during steam fixation. Fixation is by continuous steam treatment at atmospheric pressure of 100–105°C for 30 min or in pressure steam of 3.5 kPa (∼25 mmHg) 108°C for 1 h.

In afterscouring, a cationic surfactant can be used to prevent redeposition of dye on unprinted areas. A synthetic tanning agent can be applied to improve wetfastness properties of the print.

Fiber-Reactive Dyes. This class represents the main dye group for cellulosic fibers, ie, cotton and rayon. Depending on the different levels of reactivity and affinity of the dyes to cellulose, and on the available equipment, a number of different fixation methods can be used. The selection of suitable thickeners is important because of the ability of the fiber-reactive dyes to react with the hydroxyl groups that are found in traditional thickeners such as starch. This reduces efficient use of dye, makes removal of the thickener after printing difficult, and gives the print a harsh handle. Sodium alginate is the preferred thickening agent.

For steam and dry-heat fixation, an “all-in” paste contains 5–30 wt% urea and 2–4 wt% soda ash or sodium bicarbonate. As with disperse dyes, sodium m-nitrobenzenesulfonate may be added to avoid dye reduction. Dyes of low reactivity must be used to give the print paste sufficient shelf life before dye hydrolysis takes place to any appreciable extent, since several hours may pass between paste preparation and application. Fixation in steam of 100–105°C takes 2–8 min; in superheated steam of 150–180°C, 1–5 min; and in dry heat of 150–200°C, 1–5 min.

In so-called wet fixation, or two-stage, methods, the print paste containing 5 wt% urea and no alkali is printed and dried. For fixation, the prints are passed through a solution of strong alkali, such as caustic soda, potassium carbonate, soda ash, or sodium silicate. The prints are then fixed by steaming for 20s–2 min. or batching for 6–24 h. In all these cases conditions must be controlled so that bleeding of dye via the alkali solution onto unprinted areas is avoided.

As with the application of reactive dyes in dyeing, the final step is the removal of hydrolyzed (unfixed) dye in a washing operation. Since the application is from such a low effective liquor ratio, good fixation is obtained even with dyes of low substantivity: such low substantivity makes washing off easier, and dye manufacturers offer reactive dyes with these characteristics specifically for print application.

Vat Dyes. Vat dyes yield prints on cellulosic fibers with excellent fastness properties. They are used to print furnishings, drapes, and camouflage where their infrared reflectance resembles natural terrain and foliage. Like reactive dyes, their application can follow two different procedures: with all the chemicals necessary for fixation in the print paste (“all-in” or one stage), or a separate application of fixation chemicals to the dye-only printed fabric immediately before fixation.

Azoic Dyes. These are used to produce cost-effective heavy yellow, orange, red, maroon, navy blue, brown, and black shades, and are printed alongside other dye classes to extend the coloristic possibilities for the designer. Two approaches are adopted. The common method in the United States is to use both a naphthol derivative and a stabilized color base, usually in the form of a diazoimino compound in the same print paste. These stablized mixtures of diazonium salt and coupler were originally produced under the commercial name "Rapidogen", and this name is still used to describe them, and the prints produced. This mixture is soluble in dilute caustic soda and no coupling takes place at this stage. The dried prints are passed through steam at 100–105°C that contains acetic and/or formic acid vapor. As neutralization takes place on the print, the coupling occurs rapidly and the insoluble azoic dye is formed.

The alternative approach is to pad the fabric with the alkaline naphthol and dry, followed by printing diazonium salts or stabilized diazonium salts directly onto this prepared fabric. Coupling is instant and the only further treatment needed is to remove all the uncoupled naphthol and surface azo pigment in a subsequent washing treatment. Because the choice of colors is limited from one naphthol component, other shades are obtained by using other classes of dye, such as reactives, alongside the azoic colors. This approach is widely used in the production of so-called "African prints".

Basic (Cationic) Dyes. The use of basic dyes is confined mainly to acrylic fibers and as complementary dyes for basic-dyable polyester fibers. They can be applied to silk and acetate as a means of achieving bright prints, but have very poor wet fastness on those fibers.

Basic dyes are used in powder or liquid form and are incorporated into the print paste by dissolving powder dyes first in water with the aid of a dye solvent, eg, thiodiethylene glycol, and an organic acid, eg, acetic acid, followed by addition of a suitable thickener. Liquid dyes can be added directly to the thickener solution. Maintaining an acid pH in the print paste, and during the drying and fixation steps, is important. This is accomplished by adding 0.5–1.0% of a nonvolatile organic acid, eg, citric acid, to the print paste. In most cases, a fixation accelerator is used in the print paste.

Dye fixation is usually by atmospheric steaming at 100–102°C for 20–30 min. With modified polyester only pressure steam produces full fixation and color yield. Afterscouring is by rinsing and detergent scour. A scouring auxiliary with affinity to the fibers can be used to prevent redeposition of rinsed out dye.

Other Dyes. A few selected direct dyes are used to complement the acid dyes in printing of polyamide. Printing of cellulosic fibers with direct dyes is of little importance: the dyes have sufficiently low wet fastness that the washing off process and laundering in subsequent use tend to desorb dye that then migrates to unprinted areas. Sulfur dyes are rarely used in printing: their dull shades are too limiting in design possibilities. The calico printing of the nineteenth century was heavily based on the use of mordant dyes, especially alizarine (from madder) (67), and a few synthetic mordant dyes survived for special shades until the 1970s, but they have little importance today. Ingrain colorants that produce phthalocyanine dyes in situ on the fiber after application of precursors has become obsolete; likewise, aniline black (an oxidation dye) survived in printing long after its use in dyeing had all but disappeared, but it is obsolete today.

Blend Fabrics and Dye Combinations. In certain cases, it is desirable to print fiber blends with dyes, rather than use pigments. In practice, this is confined to polyester–cotton or polyester–rayon blends. Several attempts have been made to commercialize the use of single dyes that will dye both fibers. Some vat dyes have disperse-dyeing properties: Heat fixation of the vat dye dyes the polyester, and subsequent flash-aging will fix excess dye onto the cotton. Similarly, some disperse dyes will, with a suitable high boiling water-miscible solvent, dye cotton. These two systems were commercialized but are currently obsolete. More often printing polyester–cotton blends with dyes involves combinations of the appropriate dye classes. The dyes of the different classes are contained in the same print paste and, therefore, are applied simultaneously in one print operation. The printer can mix the dyes, but some dye manufacturers supply premixed combinations.

Disperse–Reactive Combinations. A careful selection of both disperse and reactive dyes is necessary. Modern systems depend on the use of disperse dyes that can be cleared in alkali without any risk of staining back onto the print during clearing, eg, disperse dyes containing diester groups. Because these disperse dyes are susceptible to hydrolysis, strong alkaline fixation conditions must be avoided. Reactive dyes with functional groups that react under neutral or acidic conditions have been researched quite widely but have yet to achieve commercial success. The selection of fiber-reactive dyes is therefore based on the usual dyes that give efficient fixation under weakly alkaline conditions, eg, 1.5% sodium bicarbonate. Fixation is by high temperature steaming or thermofixation.

The use of disperse–reactive dye combinations is popular for printing polyester–viscose rayon blends for fashion fabrics where the drape, handle, and general aesthetic qualities of such fabrics are adversely affected by pigment printing.

Disperse–Pigment Combinations. These are applied from a print paste essentially similar in composition to a pigment print paste. However, fixation requires temperatures high enough to accomplish diffusion of the disperse dye into the polyester. The advantage of this system over a straight pigment print is better fastness to abrasion and washing.

Disperse–Vat Combinations. These require a two-step fixation. The disperse dye is fixed first, usually by dry heat, followed by impregnating of the textile with an alkali and reducing agent solution and short steam fixation for the vat dye. The selected disperse dyes fixed in the polyester fiber are not destroyed by the reducing agent, but disperse dye remaining on the cellulose is destroyed.

12.3. Styles of Printing.

Direct Printing. This is the simplest technique and accounts for the majority of printed fabrics good. In this style, the print paste is applied directly onto the white prepared fabric. Each color requires its own print paste and application and colors are printed immediately after each other without (except in the case of hand screen printing) intermediate drying. This method is also called “blotch printing”, referring to the background shade of a design: The details are referred to as “pegs”. In direct printing, the blotch and pegs are printed in separate operations, and the fit is rarely perfect. In practice, designs allow for a “trap” (overlap) of blotch and peg to allow for slight imperfections of fit without producing a white “grin”.

Overprinting. Printing can also be applied to fabrics that are predyed with a “ground shade”. This is useful and economical if large areas of a single color are needed, and levelness is important. If printing with dyes, oveprinting can only be used to print dark colors on light grounds, since dyes are soluble and transparent. In contrast, pigments are opaque, and have hiding power: A pigment overprint can therefore involve darker and lighter colors on any ground shade.

Discharge Printing. The limitation of direct printing is that the greater the area of the print to be covered by print paste, the darker and larger the blotch, the more difficult it is to prevent soiling and contamination of the design as a result of the pick up of color by the printing roller or screen from previously printed areas. There is also a limitation on the fineness and sharpness of the design, especially if it is a small detailed design in a large dark background.

The fabric is first dyed to give the ground shade and then printed with print pastes containing agents that will destroy (discharge) the ground shade to give a patterned effect. Dyes for the ground shade must be chosen for dischargeability. While oxidation has been used in the past to discharge dyes, the usual approach is to dye the ground shade with azo dyes and to use print pastes containing reducing agents to destroy the dye. “White” discharges can be obtained by using only reducing agent, while “illuminated” (colored) discharges are obtained by including a dye stable to the reducing agent in the print paste. After printing the fabric is usually steamed when the ground shade is destroyed and the illuminating color is fixed at the same time. Producing the color in the discharged area in one step also leads to a perfect fit of the figure in the ground that is never achieved in direct printing, and the fine white edge to the colored design accentuates the detail. Excessive bleeding of the discharge effect results in a larger white surround to the color, a fault known as “haloing”.

On cotton, fiber-reactive dyes give the ground shade. Sodium formaldehyde sulfoxylate or zinc formaldehyde sulfoxylate with alkali are the reducing agents used to discharge them: These will also fix vat dyes used as illuminating colors. Pigments, where insolubility prevents destruction, can also be used as the illuminating color, with an appropriate binder included in the paste.

With polyester the discharge has to take place on unfixed dye: The reduction clearing process employed on dyed polyester fabrics demonstrates the invulnerability to destructive agents of dye within the fiber. The traditional process was to pad azo disperse dye onto the fabric and after drying print with the same reducing agents as for cotton to obtain white discharge, or with combinations of nonreducing anthraquinone dyes with stannous chloride to obtain colored discharges. This process is rapidly being displaced, for environmental and economic reasons, by one using alkali-sensitive disperse dyes as the ground shade. White discharges are obtained using alkali alone, colored discharges by combining alkali-stable disperse dyes with alkali. After padding and drying, the discharge paste is printed, and the discharge effected by steaming under conditions that will provide minimal fixation of the dye. The dye is subsequently fixed by high temperature.

Resist Printing. In resist printing, print pastes are used that can inhibit the development or fixation of dyes that are applied to the textile. These resists can be of a chemical or mechanical nature, or combine both methods. The most famous resist printing method is batik, where wax is used as a mechanical resist. Of more use in large scale printing are methods based on chemical resists. For example, fiber-reactive dyes, which require alkali for their fixation, can be resisted by printing a nonvolatile organic acid, such as tartaric acid, on the textile. Colored resists are obtained by printing pigments with a nonvolatile acid. A particularly elegant method uses the different chemistries of triazine and vinyl sulfone reactive dyes: Bisulfites will prevent the fixation of the latter. Thus triazine reactive dyes can be printed with bisulfite in the paste and a vinyl sulfone dye applied over the whole fabric. The vinyl sulfone dye only fixes in the nonprint areas. Like discharge printing, resist prints give fine detailed patterns with excellent fit.

12.4. Printing Machinery. *Screen Printing.* This printing process essentially consists of the transfer of print paste through a mesh to the substrate to be printed. The screen may be made of filament polyamide or polyester fibers, or of a metal, usually nickel. The early use of silk is reflected in the term “silk screen printing”. The pattern or design is produced blocking those parts that should not transfer the print paste with an impervious material. The colors within a design are separated, and for each color a “black-on-clear” film is produced with sufficient repeats to cover the area of the screen. The film is placed on the screen, which is coated with light-sensitive material. After light exposure, the unexposed parts, having been protected by the light-impervious black areas of the film, are removed by rinsing, leaving an open mesh through which print paste can pass. The clear areas of the film allow light to pass, hardening the photosensitive coating in those areas which then remains after the rinsing process. Thus the pattern is created on the screen. To withstand the mechanical stress of prolonged printing, the hardened areas of the coating have to be very strong or have to be reinforced with suitable screen lacquer. In recent years, the use of computer-driven lasers to burn away the coating on the screen has begun to replace photoengraving methods.

For hand printing, the screens are flat and held in rigid frames. Each screen deposits only one color, and as many screens as there are colors in the design are necessary. The fabric to be printed is stretched over long tables that are covered with a blanket of layers of felt and back gray or felt- and rubber-coated material. It is important that the textile material does not move or shift during the printing process, therefore it is pinned to the back gray or glued to the blanket. The screen is placed on the textile material and the print paste is scraped across the screen by means of a squeegee, penetrating through the open areas in the screen onto the textile. The screen is then lifted and moved along the table. Often every other repeat is printed initially, and the intermediate repeats printed in a subsequent pass. This allows for drying between applications and the avoidance of smudges. Succeeding colors are printed wet-on-dry, allowing for sharp marks. Hand screen printing is useful for designs that are produced in limited quantity (a few hundred yards or less): It is also good for designs that have large repeats.

Printing with flat screens can be mechanized. Semiautomatic systems use mechanized squeegees while still printing on a stationary fabric. On fully automatic flat-bed screen printing machines the screens remain stationary while the textile material is moved underneath the screens in intermittent steps. The textile material is glued to an endless blanket that serves as support for the textile material and which is cleaned with water once during each revolution. When the screens are in a lifted position, the blanket and the textile material with it move forward. When they are in a lowered position the squeegees perform the

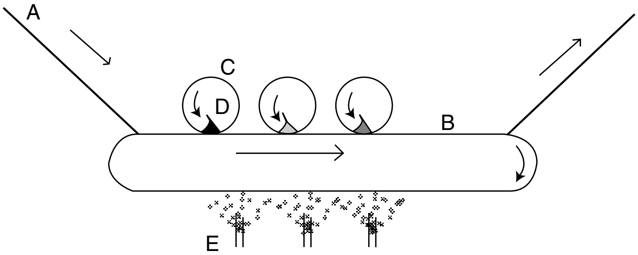

Fig. 14. Diagram of a (three-color) rotary screen printing machine. (A) Fabric, (B) Blanket, (C) Screen, (D) squeegee, (E) blanket washers.

printing. Flat-bed screen printing is widely used for the more complicated multicolored designs and is popular in Asian countries, eg, Japan. Modified versions of such machines, in which individual items are placed on arms of a circular machine and where the arms rotate under each successive screen are widely used to print T-shirts and decorative dish towels.

A major development was the rotary screen printing machine on which the screens have been fashioned into perforated cylinders. The principle was understood long before the means to produce a seamless screen was developed (63). The basic outline is shown in Figure 14.

Roller Printing. Roller printing was introduced in the late eighteenth century when the speed of production inherent in a continuous method revolutionized the textile printing industry. The design to be printed is etched into the surface of a copper print roller: hand engraving was succeeded in turn by mill engraving, the use of a pantograph machine, and by photoengraving. The last two involve an acid resistant coating on the roller: where this is removed in the desired pattern is etched in an acid (ferric chloride) bath. The fabric to be printed passes between a central bowl and the engraved print roller, absorbing print paste from the engraved areas of the print roller.

While roller printing produces designs with half-tones, fine lines and details very well, this advantage is now challenged by fine-mesh screens. The machine is massive, and changing from one colorway (color combination in a given pattern) to another, or one design to another is a slow process. Running such a machine is highly skilled, and there are high capital costs associated with storing designs on engraved copper rollers. For these reasons, the roller machine is rapidly becoming obsolete.

12.5. Other Print Methods.

While most printing is carried out using the methods described above, some alternative methods have been used or are in development.

(Heat) Transfer Printing. This method employs the intermediate step of printing dye onto a temporary substrate, usually paper. The dye is transferred to the textile while printed paper and textile are in close contact. The method has only achieved commercial success with disperse dyes, since they are transferrable via sublimation using dry heat. Short runs of textile can be printed as needed from paper held in stock (69).

Ink-Jet Printing. This technique was developed for printing on paper and is only a viable method when controlled by computer (70). Much attention in recent years has focused on the application of inkjet printing on textiles. Ink jet printing relies on the application of discrete drops of colorant solution or dispersion. The technologies are divided into drop-on-demand (DOD) and continuous inkjet (CIJ) types. In the former, drops are generated from the printhead as needed, and the impetus for the jet may be thermal, piezoelectric valve jet (air) or electrostatic. The CIJ methods produce a stream of ink droplets some of which are deflected onto the substrate: deflection may be electrostatic or via air jets. The various DOD and CIJ methods vary in the resolution, speed, reliability and cost, and the market has yet to decide which is to dominate. An air-jet CIJ method was used in an early and widely used ink jet printing method for carpets and upholstery fabrics: the large droplets needed for the heavy substrates limited the resolution.

Most development work in the 1990s and beyond has concentrated on the application to flat textile substrates. The method can provide prints of fine resolution, and unlike other roller and screen printing methods, does allow for the mixing of colorants reliably on the substrate: a full gamut of colors can thus be achieved with the four process colors (CMYK, cyan, magenta, yellow and black) although systems that use more colors can extend the gamut somewhat. A major advantage is the ability to print a design direct from an electronic file without the need to prepare, for example, a screen or a roller. For successful printing, substrates must be carefully prepared, and inks carefully formulated. Considerable challenges lie in making an ink that can be successfully jetted, and still provide fabric with sufficient fastness properties.

The chief limitation of the method has been the slow speed: some two orders of magnitude slower than conventional textile printing. This comparison relates to real-time production speeds. However, the “speed” from design to fabric with no screen preparation is much higher than with traditional printing methods. The method has therefore been mostly used as a means of providing “strike-off” prints: short example runs of prints from which customers can make bulk orders. Only then would printers order screens, thus avoiding the wasteful expense of making screens for designs that are not to be produced in bulk. It is important to render such strike-offs in a form that is achievable with screens. Ink jet printing is also obviously useful for designs that are only to be produced in short runs, and thus challenges some of the outlets for traditional hand screen printing. In the meantime, manufacturers of ink-jet systems for textile prints are continuing to develop faster machines.

Xerography. Research that sought to eliminate water from textile coloration and finishing included an examination of achieving printed designs on textile substrates (71). A colored “toner” (thermoplastic binder plus colorant) can be attracted to charged (pattern) areas of a photoconductor, which is then placed on contact with the substrate. Limitations in the production of toners that give wide color gamuts, good hand and good fastness, and the variable nature of substrates have prevented this technique from achieving commercial viability.

13. Paper Coloring

13.1. Overview. The principal reasons for coloring paper are for aesthetic appearance and utilitarian purposes. Aesthetic appearance includes colored background for printed material, colored writing papers, colored household products to harmonize with interior decor, and many other diverse uses dictated by individual tastes. Utilitarian purposes include identification of multicopy forms, identification of manufacturer or marketer of specific materials or products, opaqueness or hiding power of packaged material, or to control consistency of paper manufactured from various colored raw materials.

Paper is a cellulosic material, and the dyeing of paper shares much with that of a cellulose fiber such as cotton. The principal differences between textile and paper cellulose coloration lie in the various other components present in paper. The cellulose for paper varies more in its purity than do the textile forms of the polymer (cotton, viscose rayon, lyocell etc), the difference usually being based on the source of the pulp: chemical, mechanical, bleached, or unbleached. Sizing additives may also be present in the pulp. Differences also include the forms in which the materials may be colored. Textiles, as has been discussed, may be colored at any point in their production chain. Dyeing of finished paper is usually impracticable from technical and economic reasons, and paper coloration is confined almost exclusively to the inclusion of color in the manufacturing process. It might be thought that as a highly disposable item, high fastness levels are not required on paper: certainly paper is not laundered. However, some paper items are required to withstand exposure to light, and transfer to items with which paper comes into contact is unwelcome. It is important that the dyes used have some substantivity for the cellulose pulp, to provide the needed fastness, and to avoid color contamination of the waste water (backwater) from the manufacturing.

13.2. Colorants for Paper. Synthetic organic dyes dominate paper coloration as they dominate the coloration of textiles. The general requirements have been summarized (72). These include applicability at low (<45°C) temperatures, rapid uptake and good build up at near neutral pHs with little opportunity for the use of auxiliaries, and low cost. While many textile dyes are supplied as powders, the continuous application of dyes to paper makes liquid forms preferred. Direct dyes represent the majority of the dyes used, and with basic dyes make up 90% or more of the market. Acid dyes are also used. Pigments have been used in the past: they do not react chemically with the fiber, but are fixed physically and are dependent on filtration, absorption, occlusion, and flocculation. Paper dyeings with pigments have outstanding fastness properties, but poor affinity, low tinctorial strength, and two-sidedness problems limit their usefulness.

Acid Dyestuffs. They are used for paper that does not require wetfastness, such as construction grades, and are most suitable for calendar staining or surface coloring because of their solubility and brightness of shade. With increased environmental concern, their use has declined, since they readily stain the backwater.

Direct Dyestuffs. As expected from their use on cotton, direct dyestuffs generally have a high affinity for cellulose and are therefore the most useful dyestuff type for unsized or neutral pH dyeings. Their bonding ability to nonligneous pulps and excellent fastness properties to light and bleeding make them useful for all fine papers. The shades of direct dyestuffs are not as bright as those of acid or basic dyestuffs and in blended furnishes (bleached–ligneous pulps) mottling or graniting may occur.

Basic Dyestuffs. Basic dyestuffs have a high affinity for mechanical pulps and unbleached pulps that have a large number of acid groups (—COOH from lignin and —SO_3H from sulfite digestion) present. The cationic dyestuff interacts with these acid groups to produce, by salt formation, stable lakes that are insoluble in water. Nevertheless the addition of alum with or without sizing offers advantages depending on the depth of shade and type of paper required. Traditional basic dyestuffs have brilliant shades with high tinctorial strength, and on these pulps produce good fastness to water, steam, and calendering, and low backwater staining. Basic dyes have been modified to reduce the backwater staining when applied to pulps of lower acid group content (ie, those that have been partly bleached). Basic dyestuffs are usually used for dyeing of unbleached pulp in mechanical pulp such as wrapping paper, kraft paper, box board, news, and other inexpensive packaging papers. Their strong and brilliant shades also make them suitable for calendar staining and surface coloring where lightfastness is not critical. Basic dyestuffs have poor lightfastness, and because of their poor affinity for bleached pulps, have a strong tendency to mottle and/or granite in blended furnishes with ligneous pulps.

13.3. Dyeing Processes for Paper. Paper may be colored by dyeing the fibers in a water suspension by batch or continuous methods. The classic process is by batch dyeing in the beater, pulper, or stock chest. Continuous dyeing of the fibers in a water suspension is more appropriate to modern paper machine processes with high production speeds in modern mills. Solutions of dyestuffs can be metered into the high density or low density pulp suspensions in continuous operation.

Paper may also be colored by surface application of dyestuff solutions after the paper has been formed and dried or partially dried by utilizing size-press addition, calendar staining, or coating operations on the paper machine. In addition, paper may be colored in off-machine processes by dip dyeings or absorption of dyestuff solution and subsequent drying, such as for decorative crepe papers.

All dyestuffs and pigments are taken up more readily by the paper fiber in the acid pH range. Aluminum sulfate (papermakers' alum) is more effective than acid in fixing acid and direct dyes or pigments. The aluminum ion forms salts with acid and direct dyes that do not readily dissolve, whereas with pigments the triple positive charge also ensures fixation on the negatively charged fiber. With bleached pulps, only direct dyestuffs may be used to color unsized or alkaline-sized papers. For household tissues of deep shades to be made at neutral pH (no alum), only a selection of direct dyestuffs with particularly high affinity can be used. Blended furnishes of pulp (bleached–ligneous) can be colored successfully with combinations of dyestuff classes such as basic and acid, direct and acid, and direct and basic dyes. Generally, the dyestuff with the greatest affinity should be added first and solutions of the cationic dyes cannot be mixed with solutions of anionic dyes.

14. Dyeing of Leather

14.1. Overview. Leather (qv) is a less homogeneous product than textiles or paper. It is derived from protein collagen (skin or hide substance) treated with one or more tanning agents. The chemical characteristics and properties of collagen have been accurately determined, and leather retains properties associated with the parent substance that affect, and in many ways limit, the dyeing properties of the final product. However, the detailed chemical composition of leather is less certain, and varies considerably. Many different chemicals are used to convert the hide into leather and together with the differences in the quantities used, the method and conditions of application, and the physical condition of the hide prior to tanning or dyeing, leathers of widely varying properties are produced. Chief among these properties are sensitivity to extremes of pH, thermolability, and the tendency to combine with acidic or basic compounds. The coloration of leather has been reviewed (73).

Leather has, compared to textile substrates, a more three-dimensional character with a thickness that prevents full penetration of most colorants: the extent of penetration is thus a variable in practical dyeing. The two sides (grain and flesh) of a leather also differ in their uptake of dye. The application of colorants can therefore vary with the needs of the final product: A one-sided coloration emphasizing the grain side, a more fully penetrated coloration for clothing or upholstery, or coloration for suede products.

14.2. Tanning. Leather may be produced by use of chrome, vegetable, aldehyde, syntan, oil, and many other tanning agents. Chrome-tanned leather accounts for the greater part of leather production, but chrome is seldom employed alone. Chrome is usually employed first, and then a vegetable, syntan, or resin “retannage” follows. Vegetable tannage is employed to a fairly large degree for specific types of leather. Syntans and aldehydes, eg, glutaraldehyde, are applied combined with chrome or vegetable agents, or as a retan or second tannage over either the chrome or vegetable agents.

Practically all chrome grain leather, used mainly for shoe or garment leathers, is given a retannage with a comparatively small amount of vegetable extracts such as quebracho, wattle, or other wood extracts, or syntans, resin-tanning materials, or possible combinations of two or all three. Such an anionic retannage not only imparts desirable characteristics to the leather, but also promotes more level and uniform dyeing. The use of an anionic retannage also tends to increase the penetration of the dyes into the leather, although full or complete penetration of dye is rarely accomplished in this manner. Larger percentages of dye are therefore required for such retanned leather to produce approximately the same full shades as on untreated leather.

14.3. Colorants for Leather. The main classes of dyes employed in the coloring of leather are the acid, direct, and basic types. On chrome leather, direct dyes usually have greater affinity and produce fuller or heavier shades than do acid or chrome dyes. Acid/direct dyes as well as the metallized-type dyestuffs may be classified for the purpose of leather dyeing as the main types in use. Basic dyes color chrome leather weakly and unevenly, unless the leather is first mordanted or retanned with suitable materials, such as vegetable tannin, syntans, or previously applied acid and/or direct dyes. They may be used alone on vegetable-tanned leather to produce full shades or, as is done more frequently, following a preliminary coloring with acid or acid/direct dyes. In the latter case, basic dyes are used to impart fullness of shade with minimum coloring matter and cost.

Acid and direct dyes vary considerably in their penetrating properties on chrome leather. Although it is not possible to make a distinct division, the direct dyes as a class are more surface dyeing than the acid dyes. There is an apparent relationship between the number of sulfonic acid groups per dye molecule, the gross molecular weight, and the ability to penetrate into the interior sections of the leather. Thus, dyes with a low molecular weight and a relatively greater proportion of sulfonic acid groups penetrate more deeply than those with either a higher molecular weight or with fewer sulfonic acid groups per molecule. Since the direct dyes fall within the second category, they tend to dye only the surface of chrome leather.

As with textiles, in leather dyeing it is usually necessary to employ two or more dyestuffs to produce a given shade, and the components of the mixture should be compatible; this is an important factor in the adjustment of shades. However, the performance of a series of dyes on textiles cannot be used as a guide for their use on leather. For most leather, only superficial dyeing or surface coloring is required. However, some show and garment leathers require a certain degree of penetration, and if this cannot be obtained by simply increasing the degree of neutralization, or the addition of alkali, it may be accomplished by blending surface-coloring dyes with penetrating-type dyes.

In the case of almost all grain leather, except for special leathers, such as glazed calf, glazed kid, and all suede leather, the dye used is applied as "bottom" color and the final shade and finished product are obtained by the application of "top" coatings of pigment finishes. The greater opacity of pigments tends to fill and conceal the many imperfections, eg, those caused by insect bites, barbed-wire scratches, etc, that are normally present on average hides. An exception to this practice is the so-called aniline-finished leathers on which little or no pigment-type finishes are employed. In this type of leather, which is competing against the synthetic leathers, the greater transparency of the dyestuffs reveals the true grain-surface structure of the skin much more strikingly than do pigment finishes. A more rigorous selection of stock is necessary for this type of leather in order to avoid surface defects which are normally obscured by pigments.

14.4. Dyeing Processes. The methods used in dyeing leather are quite simple and they obtain their names from the equipment employed, such as drum, wheel, paddle, brush, tray, or spray dyeing. Most leather is dyed in drums. Drum dyeing is carried out in revolving cylinders ranging from ~1–1.5 m in width and 2.4–3.7 m in diameter. Dye and other solutions are fed into the rotating drum through a hollow axle or grudgeon. This method of dyeing is relatively rapid and efficient, as it permits the coloring of large amounts of leather in comparatively small amount to solution, with attendant low utilization of dye and other materials. The amount of solution in drum dyeing ranges from 1 to 2 times the weight of wet leather or from 4–8 times the weight of dry leather. The usual practice is to employ the necessary quantities of dyestuff, which range from 0.10 to 5.0 wt% of the blue (ie, wet) stock for grain leather. Dyeing is carried out at 46–52°C. Formic acid is used to exhaust the dye: Typically around half the weight of dye is added as 85% formic acid.

Dyeing can also be carried out in hide processors or automatic stainless steel dyeing machines with a Y-shaped cross-section to subdivide the interior into three loading sections, somewhat similar to modern garment dyeing machines.

Spray dyeing also accounts for the coloring of large amounts of leather. Usually acid or basic dyes are selected for good solubility and level dyeing properties. At present, proprietary ranges of premetallized or basic liquid dyes are available and used widely. Spray dyeing is applicable to almost any type of leather where deep penetration is not required, and is the most economical method of applying a dye.

15. Fastness Tests for Textiles

In an age of consumer activism and increasing international trade, test methods and procedures assume more and more importance. Generally accepted tests, instruments, and standards provide a common basis for the evaluation of quality in dyed textiles. Dyed textiles are evaluated with regard to their fastness (resistance to changes in color or propensity to stain other materials) when challenged by destructive agents, cleaning treatments or general use. Tests are designed to standardize or mimic these conditions in a laboratory setting. Such tests are often accelerated, ie, they predict the fastness properties exhibited by the material over a lengthy period of time in a laboratory test of short duration.

The satisfactory performance of a textile item derives from more than the durability of its coloration, and a myriad of other properties can be tested: the tests to be used for a particular item, and the level of performance required on those tests comprise the specification that an item has to meet.

The principal active bodies in the field of colorfastness testing have been national bodies such as the American Association of Textile Chemists and Colorists (AATCC). Increasingly, tests are becoming standardized across international borders and The European Community (through the Europaische-Convention für Echtheitprüfung/Groupement d'Etudes des Commissions Européenes pour la Soliditié (ECC) and the International Organisation for Standardization (ISO) have been active in promoting international versions of tests: The ISO subcommittee concerned with colorfastness tests is ISO TC 38(SCI). These various standard setting organizations produce standard test methods. The setting of specifications that detail the tests to be used and the result that represents a pass–fail level on these tests is a matter to be resolved between buyer and seller. The organization that promulgates these tests typically has subcommittees whose purview is one or more test. Tests are continually monitored for suitability, validity, etc, and any confusions in the written procedure resolved by editorial changes: methods are thus revised or reaffirmed on a regular (usually 5 year) basis, and a date suffix to the test number indicates when this was last carried out. Listings of tests are available most simply via web sites, such as those for AATCC or ISO (74,75). Several books eg, (76) provide a good overview of such testing. For detailed information in English, reference can be made to the most recent of AATCC's yearly technical manuals (77). Described below are the general principles for the tests.

Colorfastness refers to the resistance of the textile coloration to the different agencies, eg, light or chemicals, to which these materials may be exposed during manufacture or subsequent use. A lack of fastness may be due to destruction of the colorant. This is exemplified by the effects of sunlight or bleach, and only the change of color of the substrate is of interest. More often, (washing, exposure to water, perspiration etc) the color is removed, and is available to stain uncolored adjacent materials, and in these cases both the change of color of the substrate and the extent of staining of a white material are measured. In some cases, only the staining of a white material is of concern (eg, rubbing). Color change and staining of undyed adjacent fibers are assessed as fastness ratings on standard gray scales. While the principle is the same, gray scales developed by different bodies vary in detail and are not interchangeable. The basic scale to measure color change comprises five pairs of nonglossy gray color chips. One member of the pair is a constant gray, while the other is a gray of increasing difference from the standard. The pairs thus illustrate increasing perceived color differences, and these differences correspond to decreased fastness ratings 5, 4, 3, 2, 1. Scales illustrating the half steps between the basic levels (ie, 4–5, 3–4, 2–3, 1–2) are also available. To assess the staining of a white material a similar scale is used, except that the constant color is white. In both cases, the chips used are specified colorimetrically. Fastness is assessed by placing a specimen of the original, untested fabric alongside the tested fabric and comparing the difference between them to the gray scale pairs: The gray scale pair that has the same perceived magnitude of difference is chosen. The fastness of the coloration is then given the value corresponding to the chosen gray scale pair. A value of 5 means no change has occurred to the original sample, or no stain has been found on the adjacent. The lower the value <5 the poorer the fastness. This assessment has traditionally been a visual one, and thus influenced by the variability, skill and experience of the observer. Increasingly, the assessments are made via colorimetric measurement. The need to maintain the gray scales as the reference for measurement mean that such instrumental assessment is not simply based on the usual color difference scales (CMC, CIELab, etc.) but unique formulas have been developed and recommended as standard procedures (Evaluation Procedure 7 in Ref. 77).

15.1. Fastness to Light. While most fastness properties are assessed on a 1–5 scale as outlined above, exposure to light is assessed by comparing the change in color of the test specimen with that of blue wool references and is given the rating of the reference that fades most like the test specimen. This is assessed when the standard has faded to step 4 for of the gray scale for color change. In Europe eight reference samples (1 low, 8 high lightfastness based on selected dyes that give a stepwise fading scale) are used and the rating assigned the appropriate number (1–8) In the United States a different set of standard blue wool references are used (based on blending dyes so that each higher numbered sample is fading at half the rate of the preceding lower numbered sample), and while exposure is continued to the same point (gray scale step 4) the fastness is assessed by quoting the amount of exposure (in AATCC Fading Units, or, colloquially, “hours”) required to produce that change. Different results are obtained by the two procedures. For both sets of blue wool fading standards, difficulties in obtaining the dyes involved mean that alternative standards are being sought.

Fabrics are subjected to a wide range of light conditions: real life light exposure varies with season, latitude, altitude, cloud cover, and may or may not be behind window glass. The effects may be complicated by variation in humidity, temperature or atmospheric contaminants. Real-life light exposure is thus difficult to control, but test protocols do include real-life exposure as an option, and give details for controlling conditions as much as possible.

For controlled and reproducible exposures, some artificial light source operating under known conditions of temperature and humidity is required. To obtain results in a reasonable time, intense light is required. A carbon arc source was used for many years (and is still listed among test protocols), but the usual source today is an air- or water-cooled xenon arc. Other equipment exposes specimens to light from fluorescent tubes. Variations of the test include exposure to light under high temperatures and humidities that might occur in a car. Automotive manufacturers have tended to develop their own tests for these special requirements, and often use exposure measured in kilojoules (at a given wavelength) in the manner of other tests that relate to the effects of weather on the mechanical properties of textiles. The effect of rain, and of periods of dark can be programmed into these machine operations, and the test is then for colorfastness to weathering. Some dyes change color on exposure to light but revert to the original color on storage, and tests for this photochromism have been developed.

15.2. Fastness to Cleaning and Refurbishing Processes. Consumers subject textile materials to a wide range of washing conditions, and the range of conditions in tests reflects this. Some tests use a standard washing machine, while others simulate several launderings in a single accelerated test in which a specimen of textile in contact with an adjacent fabric is mechanically agitated in a closed vessel in detergent solution at defined temperature and time. A standard detergent, with or without fluorescent brightening agent, is used, since commercial detergents vary widely in their formulation. The agitation is often increased by the use of stainless steel balls in the vessel. The adjacent fabric can be a multifiber strip that includes specimens of several common fiber types. The change of shade of the specimen and degree of staining of adjacents is carried out by using the gray scale after drying.

Whether a real washing machine, or an accelerated procedure, the tests can reflect a cool, warm or hot wash, or a commercial laundering, with or without bleach (either oxygen or chlorine based). In view of the variety of conditions associated with these tests, it is vital to ensure that the particular test and the conditions used are quoted along with the test result. Recent test development has focused on the changes that can occur after as many as 20 washes, especially those containing oxygen bleach (78).

Heat Treatments and Hot Pressing. Heat exposure, as a result of ironing or other hot conditions can cause color change, and fastness tests to simulate these have been developed. A similar test simulates steam pleating.

Dry Cleaning. In colorfastness to dry cleaning, a specimen of the textile is placed in a cotton fabric bag together with stainless steel disks and agitated in perchloroethylene and the effect on the shade assessed using the gray scale.

15.3. Fastness to Other Agencies. *Other Wet Agencies.* Textile materials are subjected to a variety of aqueous media that can cause loss of color or staining. Several of these are mimicked by wetting the test material and an adjacent material with the medium of interest, placing them between glass or plastic plates, and exposing them to standard conditions (often body temperature) for several hours. These tests include those in which the medium is plain water, or water containing solutes designed to simulate sea water or perspiration. As usual, the change is assessed after drying by use of a gray scale. For determining fastness to chlorinated pool water materials are agitated in a dilute hypochlorite solution, with a standard fabric that has a known response as an internal check.

Colorfastness to acids and alkalis is determined by exposing specimens to of acid (hydrochloric, acetic, sulfuric) or alkali (ammonia, sodium carbonate, calcium hydroxide) of specified concentrations by dropping onto the fabric or steeping, and evaluating the color change after a specified time of exposure and subsequent drying. Theeffect of water droplets is simulated by dropping a specified amount of water onto a fabric and assessing the periphery of the spot after drying.

Colorfastness to Atmospheric Contaminants. Nitrogen oxides, ozone and burnt gas fumes may be present in hot air that has been passed over heated filaments or from the burning of gas, coal, etc, and these contaminants are capable of causing color changes. The temperature and the level of humidity during the exposure will often change the result, and tests reflect that possibility. Exposure is typically in an enclosed chamber, and standard fabrics that fade in a known manner are used to monitor the exposure conditions.

Colorfastness to Rubbing and Abrasion. In a simple but widely used and often critical test the transfer of color from a colored fabric by rubbing is measured. A dry and/or wet white standard fabric is attached to a peg of a “crockmeter” apparatus that is lowered onto the test fabric and rubbed back and forth (or, in a variation, in a rotary manner) 10 times across the surface of the textiles under standard pressure. The stain on the rubbing fabric is then assessed (but any change of the rubbed specimen is not considered).

Abrasion of a fabric can cause the surface to become distorted and give an apparent change of color. Alternatively, the abrasion can expose undyed or lightly dyed fibers and give a different colored (“frosted”) appearance. These possibilities can also be tested by a standard abrasion test and subsequent grey scale evaluation.

16. Testing and Analysis of Dyes

16.1. Testing of Dyes for Application Properties.

As discussed throughout this article, dyes vary considerably. Tests have been developed to determine comparative dyeing properties of dyes of different classes: eg, the division of direct dyes into classes A, B, and C is based on a test. Additionally, the “same” dye from different manufacturers may differ in the way it is formulated resulting in differences of dispersability, solubility, etc, and these factors can be tested. As with tests of fastness, ISO and national agencies have developed tests that vary in their details and the reader is directed to the specific publications, eg

(77). The results from some of these tests will provide a dyer with information that can prevent costly mistakes.

16.2. Dyestuff Migration. In a continuous dyeing operation, dye is padded onto the fabric that is then dried before fixation. Any migration of dye during drying is problematic and this tendency can be tested, along with an examination of the effectiveness of agents designed to reduce migration. A piece of fabric is impregnated with dye and auxiliaries, and a watch glass placed over a portion of the fabric and the whole dried at room temperature. The degree of migration is assessed by assessing the difference between the area of the fabric that was covered by the watch glass and the body of the fabric, either by reflectance measurement or by the gray scale.

Thermal Fixation Properties of Disperse Dyes on Polyester—Cotton. This method assesses the fixation properties of disperse dyes as a function of the time, temperature, dyestuff concentration, or presence and amount of auxiliary agents. The polyester—cotton fabric is padded and dried, the cotton dissolved in sulfuric acid and washed out of the blend, and the amount of dye on the polyester component assessed by either reflectance or measuring the optical density of a solution of dye obtained by extracting the dye with boiling chlorobenzene solvent.

Dye Transfer and Compatibility Properties. The extent to which dyes migrate during dyeing is of obvious interest, and tests to determine these properties for most dye classes exist. Typically, a specimen dyed with the dye under test is treated in dyebath conditions with an undyed speciment of the same fabric. The amount of transfer from dyed to undyed fabric is assessed, either by comparison with a gray scale, or with that obtained with a range of five standard dyes and the dye under test is given the same number as the dye it most closely resembles. Tests include those for acid and premetallized dyes on nylon, basic dyes on acrylics and disperse dyes on polyester. A test that involves dyeing a test dye in combination with a series of standard dyes assesses the compatibility of basic dyes for acrylic fiber.

Dispersion Quality of Disperse Dyes. A successful disperse dye forms a fine dispersion in water that is stable throughout the dyeing process. The initial quality or any breakdown in dyeing are tested by filtration residue of the initial dispersion or after a test exposure to high temperature dyeing conditions. The time of filtration is measured, and the filter with the heaviest residue is then compared with a series of standard photographs of standard performance and rated equal to the one it most resembles (1 poor, 5 excellent). A similar test is used to assess the speckiness of a dye or pigment dispersion used in continuous dyeing.

Foaming Propensity of Disperse Dyes. Disperse dyes are usually standardized with dispersing agents that have surfactant properties. Under dyeing conditions these may cause foam. A standard weight of disperse dye is diluted in water and an addition of detergent made. The whole is then agitated in a kitchen blender at standard speed and time, and poured into a cylinder. The level of foam in the cylinder is assessed after 150 s. Dye formulations are rated from Class A (very low foam) to Class C (very high foam).

Dusting Properties of Powder Dyes. Several methods exist to test this increasingly important behavior because of the greater awareness of working conditions and good industrial practice present today. In one, a standard weight of dye is poured through a funnel into a cylinder of defined size. A wet filter paper is placed as a collar to the funnel 200 mm above the bottom of the cylinder. After 3 min the stain on the filter paper that results from the dust in the funnel dissolving on the paper, is assessed by comparing with a set of photographic standards and the dye rated from 1 (poor) to 5 (excellent). Another method drops dye into a container with a defined air-flow through it. The dust formed is sucked out of the chamber and through a filter. The dust can be assessed visually, by eluting the dye from the filter, by measuring the optical density of the solution, or gravimetrically by weighing the filter before and after the test.

Dye Solubility. Standard test procedures have been developed by ISO for the determination of cold-water solubility of water-soluble dyes; the solubility and solution stability of water-soluble dyes, and the electrolyte stability of reactive dyes.

16.3. Analysis of Dyes. Beyond the simple tests to determine suitability for application performance discussed above, dyes are subject to analysis for a variety of reasons that range from the academic to the practical. Both quantitative and qualitative data are sought, and dyes can be analyzed in substance, on the fiber, or after a suitable extraction process. At a fundamental level many of the methods used to analyze organic chemicals in general can be useful in analyzing dyes. The fact that they are colored is often helpful in the analysis. Of primary concern to this entry is the analysis that relates directly to their application. The subject has been addressed in a number of publications (13,79).

Quantitative Analysis. Since dyes are routinely standardized by dilution with electrolyte or a dispersing agent, the strength of a dye can vary widely. Accurate reproduction of dyeings relies on accurate reproduction of the dyebath, in turn relying on knowledge of dye strength. The comparison of strength of two samples of the "same" dye is fairly routine, but the matter becomes complex when qualitative differences are included, increasingly so as the quality differences increase.

Solution Spectrophotometry. The relative strength of a dye (compared to a standard) or the dye concentration in solution can be determined accurately for most dyes by this method. A uv–visible spectrophotometer is a routine piece of equipment in most laboratories, and many reflectance spectrophotometers used for color mesurement of solid (textile) substrates are capable of making transmittance measurements. The procedure is the subject of standard AATCC and ISO test methods. Solution spectrophotometry is based on Beer's law and the Lambert-Bouger law concerning the relationships between absorption and concentration of the absorbing layer. It is important to prepare dye solutions that are stable and obey Beer's law over the concentration intervals used: aggregation of dye can confound the method. The method is not appropriate for reactive dyes where hydrolyzed dye is present that absorbs similarly to the unhydrolyzed material. It is also not appropriate for sulfur dyes, and is difficult to apply to vat dyes although means to maintain dye in the water-soluble leuco form have been developed, as have solvent systems for use at elevated temperature. Disperse dyes also require the use of non-aqueous solvents: Although there is no agreement on a single solvent, acetone and dimethylformamide (DMF) are commonly used.

Reflectance Spectrophotometry. Since the ultimate utility of a dye is as applied to a substrate, the generally preferred method of evaluation is to apply the dye and examine the final results achieved. In manufacture, many dyes are standardized in solution but there is always a final control step where dyeings are prepared. Historically, such dyeings have been evaluated visually for the relative strength and the shade compared to the standard. Increasingly, the evaluations are based on objective color measurement using K/S values (or, where colorants are not identical, summations of K/S) (80,81) Reflectance spectrophotometry is essential in the case of reactive dyes when, as outlined above, nondyeing but colored hydrolyzed material is always present to a greater or lesser extent, and for sulfur dyes, and generally preferred for vat dyes. Guidelines for the use of this technique have been published (82).

Qualitative Analysis. Dyes may need to be identified for many reasons that range from the quality control of dyes in manufacture, the knowledge of a rival manufacturer's product, or (for a dyer) some assurance that the product supplied is the right one.

Paper and Thin-Layer Chromatography (tlc). These techniques are mostly useful for qualitative analysis of dyes and rely on the separation of components in an analyte as an eluent moves through a stationary phase (83–86). Paper is a self-supporting stationary phase: The technique becomes thin layer when a solid phase (silica, alumina, etc) is bonded to a support (glass, aluminum foil, plastic). The use of tlc for the analysis of dyes has been described in classic papers, and the early application of the technique for dyestuffs reflects its particular suitability for the task; it is rapid, simple and inexpensive, and in comparison with its use for analyzing colorless compounds, developers or disclosers are not essential (although occasionally useful). The tlc method is used routinely for the identification of dyes and assessments of their purity. In dyestuff manufacture the progress of reactions involving complex mixtures can be accurately followed.

On the various adsorbents a great many solvent mixtures have been propounded as eluents for the separation and analysis of dyes. In this way the analysis of all classes of dye has been suggested. The most suitable dyes for analysis by tlc on polar adsorbents are the weakly polar ones, such as disperse dyes, which have a limited solubility in weakly polar eluents such as toluene–ethyl acetate mixtures. More polar, water-soluble dyes such as acid and direct dyes, are more strongly adsorbed, and require more polar eluents that include the use of water, alcohols, esters, pyridine, ammonia, or acetic acid. A technique originally introduced in high pressure liquid chromatography has been developed for thin-layer methods. Here, the polar surface of the adsorbent is modified to become nonpolar by the bonding of alkyl chains (typically of 8 or 18 carbon atoms), hence the title of "reversed-phase" tlc. Polar (water-soluble) dyes are less strongly adsorbed, and can be eluted and separated with fairly simple polar eluents such as mixtures of water and methanol or acrylonitrile (86).

Dyes may be analyzed in substance or may be extracted from fibers. In each case a spot of dye solution is applied to the plate with a capillary pipette. After removal of the solvent used in this application the plates are developed in a tank with a suitable eluent which wicks up the plate.

The technique will separate the components of a dye mixture (recognizing that the mixture may be the result of the manufacturing reactions, or deliberately created), and dye identification is feasible: While the method can be quantified by reporting Rf values, in practice it is necessary to base the analysis on direct comparison with known dyes. When minor impurities are present the technique can become quite powerful.

For semiquantitative or quantitative analyses, the separated dyes can be measured with a reflectance densitometer or they can be extracted from the plate or paper and measured by transmittance spectrophotometry.

High Pressure Liquid Chromatography. This modern version of the classical column chromatography technique is also used successfully for separation and quantitative analysis of dyes. It is generally faster than thin layer or paper chromatography; however, it requires considerably more expensive equipment. Visible and uv photometers or spectrophotometers are used to quantify the amounts of substances present.

17. Safe Handling of Dyes

The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD), an international body of all primary manufacturers based in Europe but also with standing committees in the United States, Brazil, and Japan, issues clear guidelines for the safe handling of dyes (87). In December 1991, the United States Operating Committee of ETAD joined with the United States Environmental Protection Agency in publishing a pollution prevention guidance manual for the dye manufacturing industry (88). Most countries have health and safety legislation that covers the way in which industrial chemicals are handled, and dyes and dyeing auxiliaries are covered under these regulations (see also DYES, ENVIRONMENTAL CHEMISTRY).

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