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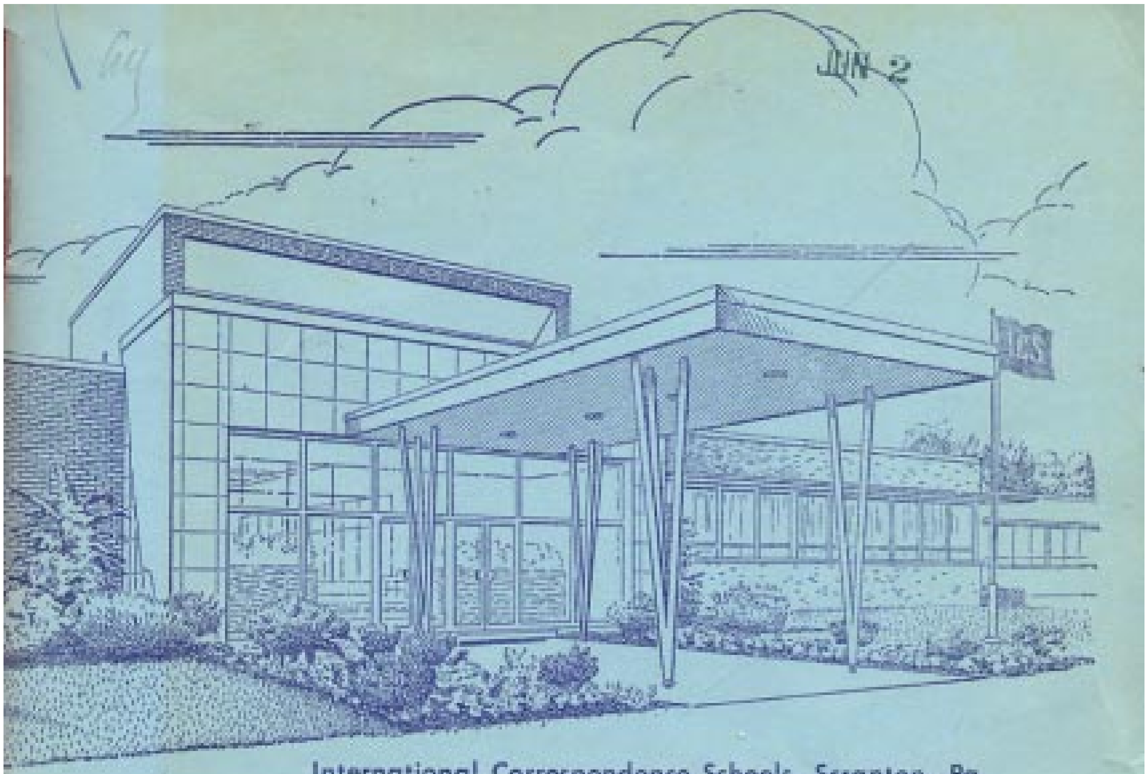

International Correspondence Schools, Scranton, Pa.

Textile Dyeing

By

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Member, American Association of Textile Chemists and Colorists

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E. I. du Pont de Nemours & Company

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International Correspondence Schools, Scranton, Pennsylvania
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YOUR TECHNICAL EDITOR

This series of texts, *Textile Dyeing*, Parts 1, 2, and 3, has been technically edited by Raymond C. Gagnon, Consultant for the School of Textiles, in which the instructional service for these texts is provided. In editing these texts, Mr. Gagnon's aim has been to ensure that the material presented to the student meets the high standards of technical accuracy, ready application, completeness, and readability to which every ICS text must conform.

Mr. Gagnon attended the Rhode Island School of Design. His background includes fifteen years of practical experience in a New England synthetics mill. He is a member of the American Association for Textile Technology and the American Association of Textile Chemists and Colorists.

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PART 1

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What This Text Covers . . .

Here is a brief outline of the contents of this text. Use the outline to check off each section as you study it. Then you will know with which section to begin when you pick up the text again.

1. Theory of Dyeing . . . . Pages 1 to 8
   You are introduced to the subject of dyeing by learning about its development and the factors to be considered. Then you are taken through the various methods by which cotton can be dyed.

2. Dyeing Machinery . . . . Pages 9 to 19
   Here you will learn about the various types of machinery used in the dyeing of cotton. Included in the group are the dye box, rotating-arm machine, padder, dye jig, dye beck, machines for continuous processing, and many others.

3. Direct, Sulfur, and Naphthol Dyes . . . . Pages 20 to 41
   Direct dyes are perhaps the most common type used on cotton goods. In this section you will study about these dyes and the manner in which they are applied to cotton goods. Then you will learn about sulfur and naphthol dyes and how they are used on cotton goods.

4. Vat Dyes . . . . Pages 42 to 50
   Here you will learn how vat dyes are used in the dyeing of cotton goods.

5. Indigosols, Basic Dyes, and Oxidation Colors . . . . Pages 51 to 53
   Brief descriptions of the indigosols, basic dyes, and oxidation colors, and the manner in which they are used make up this section.

6. Mordant and Fiber-Reactive Dyes . . . . Pages 54 to 57
   The text concludes with a brief coverage of mordant dyes, followed by a fairly comprehensive discussion of fiber-reactive dyes.

Textile Dyeing

PART 1

Theory of Dyeing

History of Dyeing

1. A review of the history of textile dyeing shows that the art of textile dyeing develops on four fronts: the artistic, mechanical, chemical, and technological. Sometimes one front forges ahead, leaving the others to catch up as best they can.

During the long centuries preceding the Industrial Revolution, the artistic front strode far ahead. The ancient Egyptians produced colored linen cloths of fine construction, and in the Far East the Indians and Chinese were known to have worn cloth colored with the natural dyes of the time: red, from madder root and called alizarine by the Arabs, and blue, obtained from woad or indigo. The fine linens of Biblical times were dyed with the purple which was secured from the sea snail, or murex, with the yellow from fustic and weld; wools were dyed with the red from the kermes and cochineal insects. The methods used in applying these dyes were based entirely on practical experience.

From about 1780 until 1860, mechanical means were invented to save hand labor, and in these busy years of the Industrial Revolution, the mechanical front far outstripped the other fronts. With Perkins' discovery of mauve, the first synthetic dyestuff, it was the chemists' turn. Other discoveries produced new dyes. Whole new groups of dyes were created. The fast vat dyes came into being about the end of the nineteenth and beginning of the twentieth century, followed by the valuable naphthol dyes early in the twentieth century.

In time, the natural dyes were synthesized, and were gradually supplanted by manufactured colors. Today very few natural dyes are used. But in the manufactured class there are hundreds of different dyestuffs of many different groups. Up until about 1950, then, the predominant front was the chemical.

Today we stand at the threshold of a new technology. Man's ingenuity has created many synthetic fibers, such as nylon, Orlon, Acrilan, Arnel, Creslan, Dacron, all with excellent physical properties and all requiring special technology to dye them properly. Other new advances include dyes which react chemically with the fiber, fiber-reactive resins and finishes, and such scientific dyeing methods as pad-steam fixation of vat dyes and "thermosol" dyeing of polyester fibers. Above all, a whole new technology of the art of dyeing is evidenced in the use of spectrophotometers to describe accurately any given dyestuff by its spectrograph, and in the use of computers to match any desired shade from the spectrographs of available dyestuffs.

Terminology

2. Acquaintance with the fundamental terms used in dyeing is necessary to a study of the art of dyeing.

Dyes, or dyestuffs, are organic substances which impart to textile fibers and fabrics, and other materials, color that is relatively stable, or fast, to washing and light.

Dyeing is the process by which color is imparted to a material in a uniform manner, and in which the dye becomes a part of the material. Painting is not dyeing, because the pigment in the paint merely adheres to the surface of the fiber.

In textile dyeing, a small amount of dye will color a comparatively large amount of material because the fiber absorbs, or exhausts, the dye from the liquid in which it is distributed. Thus dyeing is different from staining, which occurs when a piece of cloth is dipped in berry juice.

As covered in this course, dyeing applies to the coloring of textile fibers and fabrics, although many other materials are dyed today. Among these are paper, leather, gasoline, plastics, buttons, feathers, foam rubber, furs, food, and cosmetics. Aluminum is dyed with water-soluble dyes. Dyes are also used to color inks, varnishes, coatings, and paint.

Dyestuffs may be dissolved or dispersed in a liquid and thickened with a suitable thickening agent, applied to the surface of a textile fabric, and then fixed in the fabric by steaming or other means. When the dyestuff is applied in the form of a pattern, the process is known as textile printing, which is thoroughly covered in a separate text.

Tinting is used extensively by weavers to distinguish different yarns. Dyes chosen for this application are fugitive; they are easily removed from the yarns.

Factors in Dyeing

3. The factors which influence the dyeing procedure are three in number: 1) the fiber to be dyed, 2) the dyestuff to be used, and 3) the medium in which the dyeing is to be done. Each of these factors is closely dependent on the others. For example, if the fiber to be dyed is not absorbent, it will be difficult to obtain complete penetration of the dyes. Also, if the water — which is the medium most commonly used in dyeing — is excessively hard, some of the dyes may be precipitated — that is, separated from the solution — causing specking and unevenness.

The fibers to be dyed may be natural or synthetic. Natural fibers are generally classified into two main groups, animal and vegetable, or more accurately, protein and cellulosic. The animal, or protein, fibers include wool, mohair, alpaca, and silk, to name a few. The vegetable, or cellulosic, fibers include cotton, linen, bast, jute, and the like.

Many synthetic fibers also fall into these groups. Viscose rayon is regenerated cellulose. Hence, it is cellulosic. Similarly, Avril and Zantrel are modified viscose rayon, so that they too are cellulosic. Nylon, on the other hand, partakes of many of the qualities of wool fiber, containing nitrogen groups like wool, and so can be regarded as a protein fiber in its dyeability.

Acetate, Arnel, and the polyester fibers fall into neither group. They require a special dyestuff group, consisting of the disperse dyes. Orlon, Acrilan, Creslan, and other new synthetic fibers exhibit affinities for various dyestuff groups.

4. The type of dyestuff used is determined by the specific fiber being dyed and by the fastness properties desired. The dyes are applied according to the method peculiar to each particular class of dyes. The classes of dyestuffs are as follows:

Direct Dyes. A large and important class of dyes, the direct dyes have an affinity for the cellulosic fibers from a dyebath containing salt. They also have an affinity for silk, and they stain wool and nylon. Direct dyes do not possess good fastness to washing, and therefore are often given some type of aftertreatment.

Acid Dyes. Although used mainly for dyeing wool, the acid dyes are also used to dye silk, nylon, and certain other synthetic fibers. The acid dyes are conveniently subdivided into five groups, depending on their constitution and methods of application.

1. Strong acid dyes, which require strong acid to exhaust on wool.
2. Weak acid dyes, which require only weak acid to exhaust on wool.
3. Chrome dyes, which require treatment with chromium salts.
4. Acid premetalized dyes, fast dyes which require strong acid to exhaust on wool.
5. Neutral premetalized dyes, fast dyes which are dyed without acid.

Basic Dyes. The basic dyes produce bright shades on wool, Orlon, Acrilan, and Creslan. They can also be used to dye cotton and rayon, provided that special prepartions are made.

Disperse Dyes. Though not soluble in water, the disperse dyes form fine dispersions. They are used to dye acetate, Arnel, the polyester fibers, and to some extent, nylon and Orlon.

Mordant Dyes. Formerly used extensively on cotton, the mordant dyes require that the material to be dyed be prepared with certain salts before dyeing. These dyes now find limited use on cotton and rayon goods.

Vat Dyes. The vat dyes produce very fast colors and are used extensively on cotton in all forms, as well as on rayon and other cellulosic fibers. They are called vat colors because they are not soluble in water and must be rendered soluble by "vatting," that is, by reducing with sodium hydrosulfite in an alkaline bath.

Indigosols, or leuco esters of vat dyes. Indigosols are vat dyes produced in a soluble form. They are used on cotton, rayon, and wool.

Sulfur Dyes. Especially suitable for dyeing dark shades on cotton and rayon, sulfur dyes are not so fast as vat dyes, but are faster than direct dyes.

Insoluble Azo Dyes. Also known as naphthol dyes, the insoluble azo dyes are ingrain colors; that is, the dye is produced in the fiber. These dyes yield very fast colors, and are used principally on cotton and rayon. However, methods have been developed whereby they can be applied to acetate, nylon, and even polyesters.

Fiber-Reactive Dyes. A very new and interesting class of dyes, the fiber-reactive dyes actually combine chemically with the fiber. They are used for dyeing and printing cotton and rayon. Some will react with nylon. They are faster than direct dyes, but not so fast as vat dyes in many respects.

Oxidation Colors. Only one dye among the oxidation colors finds any application in present-day textile dyeing. This is aniline black, produced on the fiber by chemical oxidation of aniline. It is interesting to note that fur dyeing, a highly specialized art, is done with oxidation colors.

Pigments. Strictly speaking, pigments are not textile dyestuffs, since they have no affinity for the fiber and must be bound to the surface of the fiber by resins. They are used extensively in printing, and to some extent for "dyeing" light shades by padding. Pigments are used to dye glass fibers under high temperatures. Pigments are also used to color fibers in the spin dope before the fiber is formed. This is called dope dyeing.

Each of the classes of dyes will be taken up as you study further the art of dyeing.

General Principles

5. As the listing of dyestuff classes shows, there are many different principles involved in dyeing. Direct dyes are absorbed by cotton from a bath containing salt. Acid dyes are absorbed by wool from a bath containing acid. Insoluble azo dyes are produced in the fiber, while fiber-reactive dyes actually unite chemically with the fiber.

In every case there must exist some type of affinity between the fiber and the dyestuff. This affinity depends on the chemical and physical natures of the fiber and of the dye. The same dye reacts differently with different fibers. For example, acid dyes have an affinity for wool, silk, nylon, but no affinity for cotton, whereas direct dyes have an affinity for cotton, rayon, silk, but no affinity for acetate.

It is rather astonishing that the ancient Chinese, Persians, Indians, and Egyptians knew how to obtain a red dyeing with madder, even though madder has no color of its own and no affinity for cotton. Only when the cotton is first saturated

TABLE 1

COMPONENTS OF COTTON

Substances	%
Cellulose	94.0
Protein	1.3
Pectin	1.2
Ash	1.2
Wax	0.6
Total sugars	0.3
Pigment	Trace
Others	1.4

with alum and the alum is rendered insoluble in the material will the madder have affinity for the aluminum salt, thus producing a red dyeing.

Today the many principles involved in dyeing are understood. This understanding can be applied to the better selection of dyes and dyeing techniques to improve fastness properties and promote uniformity and reproducibility of dyeings.

Cotton

6. A brief review of the physical and chemical properties of cotton will be helpful to you at this point. There are several kinds of cotton, evaluated according to staple length, diameter, tensile strength, color, twist, and evenness of the fiber. The short-stapled cottons have a larger diameter than the long-stapled varieties, and they show a greater affinity for dyestuffs. If the cotton is gathered before it is ripe, or if its development is interrupted for any reason, the result is unripened, or *dead*, cotton. The low affinity of such unripened cotton necessitates a choice of special dyestuffs.

In chemical composition, cotton is the purest form of cellulose obtainable in nature. In Table 1 are listed the substances, with their percentages, which are found in an analysis of an average grade of cotton.

Note that, of the total components, only 6% are impurities; these impurities include pectins, ash, wax, sugar, pigment, and a few others, such as albumin and cotton oil. The residue after calcination shows calcium, magnesium, and potassium. Some of the organic impurities may be the cause of faulty dyeing. The pectins have reducing properties. The cotton waxes and oils, on the other hand, hinder dyeing because they repel water. They are removable by kier boiling and bleaching.

7. Cotton is resistant to alkalis. It may be boiled under pressure in a closed vessel with a dilute solution of caustic soda. Concentrated solutions of caustic soda cause cotton to shrink, even when the goods are cold. If cotton cloth is treated with a 21% to 23% solution of caustic soda, it will shrink. However, if

the cloth is kept under tension during treatment, it will be mercerized, a fact discovered by John Mercer in 1851. Mercerized cotton shows a considerable increase in strength, luster, and affinity for dyestuffs.

Volatile organic acids, like acetic acid and formic acid, do not attack cotton, even in strong concentrations. But strong mineral acids, such as sulfuric and hydrochloric acid, are harmful. Under the influence of heat they can effect a complete destruction of cellulose, as happens in carbonization. Precautions must therefore be taken when using either strong mineral acids or the nonvolatile organic acids. Reducing agents have little effect in the normal application of dyes, but prolonged stripping will tender, or weaken, the fiber. The use of strong oxidizing agents results in oxycellulose; the strength of the fiber is thereby decreased and its chemical and dyeing behaviors are changed.

Prolonged exposure to the simultaneous influence of direct sunlight, air, and moisture will also cause oxidation of cotton into oxycellulose. On the other hand, cotton is not visibly affected by heat until a temperature of about 248 F (degrees Fahrenheit) is reached. If dried for a length of time at 220 F, cotton loses its normal humidity of 8.5%, but retains its ability to take moisture up again.

Preparation for Dyeing

8. The importance of proper and adequate preparation of cotton before dyeing cannot be overemphasized. The objectives in treating the goods before dyeing are 1) to remove all impurities which would later affect the ability of the fiber to absorb the dyestuff properly; and 2) to ensure that the fiber is in a suitable physical state to react properly to subsequent finishing operations. If these two kinds of preparation are not properly carried out, the results obtained will not be consistent for all of the batches of goods run.

A knowledge of the end use of the material is essential for the proper preparation of the fiber. For example, if the end product is to be white goods, a great deal more care must be taken to remove all impurities than if the end product is to be work clothes. In general, more care is taken with the materials that retail at a relatively high price than is taken with the lower priced materials. The material may be prepared at any one of various stages of manufacture, as in the form of raw stock, yarn, or piece goods. Natural color can be removed, and particles of seed destroyed, by kier boiling or peroxide bleaching.

Raw Stock

9. If the cotton is to be dyed in the form of raw stock, very little preparation is necessary. The addition of a surface-active wetting agent lowers the surface tension enough to permit the dyestuff to penetrate the wax and pectin. Sometimes it is necessary to clean the material to some degree. This cleaning is best done with a minimum amount of alkali, because it is desirable to preserve some of the natural wax content, to aid in the subsequent spinning operations. The carding

operation that follows dyeing of raw stock will level out any uneven dyeing that may result from insufficient penetration.

Cotton Yarn

10. Cotton yarns in the form of hanks or skeins are usually boiled out on skein arms, using 0.5% to 1% synthetic detergent and 1% soda ash. The addition of 0.5% caustic soda and 0.25% sodium perborate to the bath during the boil-off will increase the cleansing action.

An example of such a treatment for 100 lb (pounds) of yarn is the following: 1) To the liquor add 8 oz (ounces) of wetting agent. Wet out for 5 to 10 min (minutes) at 140 F. Drop the bath. Rinse the yarn. 2) To a fresh bath, add 3 oz of synthetic detergent, 3 oz of sodium perborate, and 8 oz of caustic soda. Bring to the boil rapidly and boil for 20 to 30 min. Drop the second bath. 3) To a fresh bath, add 0.25 to 0.5 oz of synthetic detergent. Boil for 5 to 10 min. Drop the third bath. 4) To a fresh bath, add 16 oz of rewetting agent. Run for 5 min at 120 F. Remove the skeins, without rinsing. Hydroextract the skeins.

If the material is to be dyed immediately, the fourth step may be omitted. After step 3, rinse well and to a fresh bath add 4 to 8 oz of wetting agent, and then proceed with the dyeing.

The usual method of accomplishing the dyeing, for 100 lb of yarn, is as follows: To the liquor add 1 lb of synthetic detergent and 1 lb of soda ash. Bring the liquor to the boil rapidly and boil for 20 to 30 min. Drop the bath, and rinse well.

Generally, the addition of a wetting agent or synthetic detergent to the dye liquor is sufficient, as the material is almost always scoured before being spun into yarn. Package dyeing is more successful if the dyestuff, wetting agent, and other necessary chemicals are mixed in the expansion tank. The mixture is then allowed to hit a dry package in the machine. This procedure prevents so-called crossovers, that is, improperly dyed yarn where the wound yarn overlaps on the package.

Cotton Piece Goods

11. The final appearance of cotton piece goods depends upon how adequate and thorough the preparation of the fabric has been. Piece goods are of two types: 1) the type that can be handled in rope form, and 2) the type that must be handled in open width. Heavy fabrics, which are subject to crease marks and rubs, must be handled in open width.

Cotton piece goods that are to be dyed continuously are usually prepared by one of the following methods: kiering under pressure, jig boil-off, or continuous boil and bleach.

In kiering under pressure, the fabric is treated with caustic soda (3% on the weight of the material) for 8 to 10 hr (hours). This is followed by a peroxide bleach or a chlorine bleach in the kier, or by a chlorine bleach outside the kier.

In the jig boil-off method, the fabric is boiled for 2 to 3 hr with caustic soda at a concentration of about 50 grams per liter. This is followed by either a peroxide or a chlorine bleach on the jig.

When the continuous boil and bleach method is used, the fabric is padded with a solution of caustic soda and allowed to set in a J-box for about 1 hr. This is followed by padding with hydrogen peroxide and standing in another J-box at 212 F for about 1 hr.

Following the bleaching process the fabric may be mercerized, rinsed, neutralized, and dried for dyeing. Fabrics which are made from combed yarns do not need bleaching unless they are to be dyed in pastel shades. The mercerization of cotton in piece-goods form adds luster to the fabric, aids in stabilizing the fabric dimensionally, and makes the immature fibers more susceptible to dyestuffs. Mercerization also increases the overall affinity for dyes.

Dyeing Medium

12. Water is the medium in which almost all dyeing is done. The water should be in a fairly pure state in order to obtain the best results. The purest state of water is distilled water, but because this is very expensive, other forms of water must be used. Most plants use city water, which comes from lakes, rivers, or wells, and which varies in the amounts of impurities present.

Chlorine, lime salts, and iron and other metals present may have a retarding effect upon the affinity of the dyestuff for the material to be dyed. There is also the danger that the impurities will combine with the dyestuff in such a way as to render it unsuitable for use. Such impurities as colloidal solids, organic matter, and sediment may be removed by filtration. But certain salts cannot be filtered out. Hard water should be made soft before use, and this treatment should precede the boiler feed and other processing.

Rainwater is soft; if rainwater runs off the soil into a stream, it generally does not have time to pick up metal salts and become hard. Well water from rocky pockets, or water that has seeped through limestone deposits, will be hard.

Hardness is measured in parts of calcium carbonate per million parts of water. Up to 50 ppm (parts per million) is called soft water, 50 to 125 ppm is moderately hard, 125 to 200 ppm is hard water, and over 200 ppm very hard. Great Britain uses a different system of grading hardness, with one degree hardness denoting one grain calcium carbonate per imperial gallon, or about 14 ppm.

Hard water precipitates soap and leaves harsh deposits on cloth. Some dyes are precipitated by hard-water salts to such an extent that their dyeability changes.

The formation of boiler scale is the result of hard-water salts in the boiler feed.

The use of soft water promotes good bleaching and scouring, good solubility of dyes, and even, well-penetrating dyeings. In areas where the hardness of the water is high, it is advisable to install a softening system, of which there are many types. The older lime-soda system has been largely replaced by the ion-exchange system.

Any lime salts not removed by these systems, or salts encountered in using soft water from streams, may be sequestered, or rendered harmless, by using such glassy phosphates as Quadrafos or Calgon, or such organic sequestering agents as Ketex, Sequestrene, and the like, in the dyebath, in scouring, and in bleaching.

Dyeing Machinery

Development and Principles

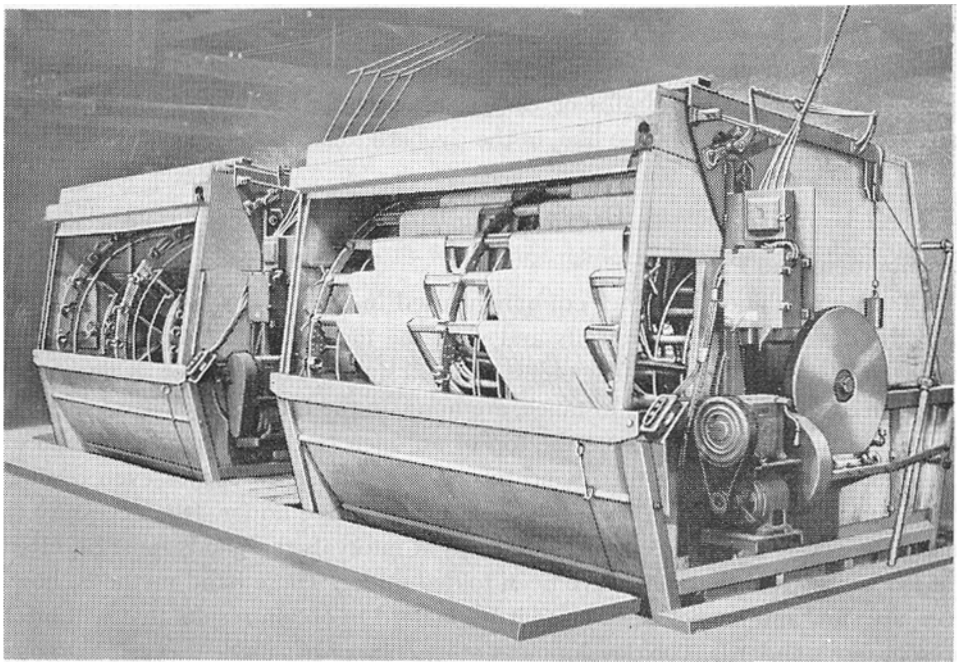
13. The machinery or other equipment used in dyeing has had to keep pace with the development of dyestuffs and with the increase in the speed, volume, and exactness of production. The oldest and still simplest methods of dyeing make use of an open tub. Yarns, for instance, are hung, in the form of skeins, on wooden sticks. The sticks are laid across the top of an open box containing a volume of dye liquor. The skeins are then hand turned periodically to ensure even dyeing. Piece goods are put into an open tub containing the dye liquor. It is necessary to rotate the goods with a wooden paddle, and at intervals the goods must be lifted out to expose areas that may have been folded under. These hand methods, however, are slow and inefficient because it is too hard to obtain results that will meet present-day standards. The development of machinery has made it possible to dye huge lots of goods rapidly and with a minimum of manpower.

There are three basic types of machines used in dyeing today. They are 1) the type of machine that moves the material through the liquor; 2) the type of machine that moves the liquor through the material; and 3) the type of machine that does both. The first type is used to dye piece goods, skeins in boxes, and hosiery in the rotary-type machine, and to dye yarn in chain warps. The second type is used to dye raw stock, yarn in the package form, and yarn by the cascade method. The third type is used to dye piece goods by a continuous method.

Dye Box

14. A simple machine called a dye box is one of the machines that move the material through the liquor. This machine consists of a long, rectangular stainless-steel box with a false bottom. In the false bottom is a series of heating pipes which may be heated by electricity or steam. The temperature of the bath is regulated by the amount of steam or electricity that flows through the pipes. Valves are present to let water into and out of the box.

With the dye box, the dyeing is usually done by hand. Yarn in skein form is placed over the wooden or metal sticks and immersed in the liquor. The sticks are systematically turned by two workmen, one on each side of the box. Care must be taken so that the skeins do not touch the bottom of the box. When the desired shade is obtained, the skeins are removed and dried. Salt rinses and after-



Courtesy of Klauder Weldon Giles Machine Company

FIG. 1. FERRIS WHEEL MACHINE

treatments may be done in the same box. Sometimes, however, it is desirable to dye further lots of the same shade in the same liquor, with the addition of more dyestuff, thus conserving time, dyestuff, chemicals, and water. When this is done, a separate machine must be used for the aftertreatments.

Rotating-Arm Machine

15. Another machine that moves the yarn skeins through the liquor is the Buhlman-type rotating-arm machine. This type of machine employs the same principles as those used in hand dyeing. The box containing the dye liquor is built on the same lines as the dye box, with a false bottom to contain the heating units. However, in place of the wooden sticks, there are mechanical arms. These arms are made of porcelain, pyrex, or stainless-steel fluted rollers. The skeins are loaded on the arms in the same manner as on the sticks in the hand method. The arms are then lowered mechanically into the liquor, where they can be rotated in alternate directions. The yarn rotates with the arms, producing even dyeings and using less physical labor than the hand method. When the dyeing is completed, the arms are raised by means of compressed air. Either the yarn is left to dry on the arms, or it is just temporarily lifted out of the bath while a liquor for aftertreating is being prepared.

Ferris-Wheel Machine

16. The skein-dyeing machine shown in Fig. 1 somewhat resembles a Ferris wheel. The large wheel, with its radial spokes, is enclosed in a metal case. The skeins are mounted on pairs of poles. One pole is fastened to the spokes across the wheel, at the circumference; the other pole is fastened near the center of the wheel. A series of such mountings are spaced evenly around the rim of the wheel, so that, when a loaded machine is viewed from the side, the yarn itself looks like the spokes of the wheel.

The wheel is lowered into the dye bath and rotated there. During each rotation the yarn is in the dye bath for one half of the time. In order to prevent marks on the yarn, each of the poles is rotated by means of gears, so that no area of the yarn goes unexposed in the dye bath. Here again, in the Ferris wheel machine, the box containing the dye liquor is of the same type as that of the simple dye box. Only the method of handling the skeins is different. This type of machine may be used for dyeing wool yarn in the hank form, as well as for cotton and rayon skeins.

Rotary Machine

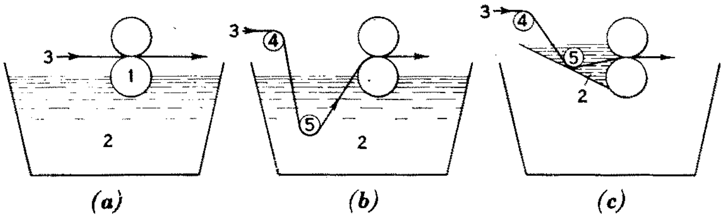
17. The rotary type of dyeing machine is used principally by the hosiery-dyeing trade. It consists simply of a drum with four arms. The drum is placed in the dye liquor and rotated back and forth. The machine is practically the same as that used in laundries for washing clothing. Around the drum is a huge perforated cylinder encased by a solid cylinder. In the solid cylinder is a door that lifts out while the goods are being placed inside and shuts watertight while the drum is rotating in the liquor. The rotary machine is also used to a great extent by garment dyers. Another type of dyeing machine makes use of a rotary paddle. The paddle moves a bag, which is filled with hosiery or other easily dyed goods, through the dyeing liquor.

Chain-Warp Dyeing

18. The machine used for dyeing chain warps consists of an open box. In the box are immersion rollers which guide the chain warp through the dye liquor. The entire warp passes through the liquor and then through a squeeze roller. Depending on the depth of the shade desired, the operation may have to be repeated several times. The dye boxes can be connected in series, or repeats can be performed in the same box. Several chain warps may go through the same dye liquor, but each set needs an individual immersion roller and squeeze roller. The whole process is similar to padding.

Padder for Dyeing

19. The padder, often used in finishing, can also be used for dyeing. With this type of machine the piece goods are dyed by impregnating the fiber with dyestuffs under the pressure exerted by a series of squeeze rolls. Padding is the fastest method to get very level dyeings on cotton cloth.



1. bottom squeeze roll
2. dye liquor
3. cloth
4. first guide roll
5. second guide roll

(*a*) Slop, or nip, padding
(*b*) Padder used in immersion dyeing
(*c*) Pad box used to carry out dyeing

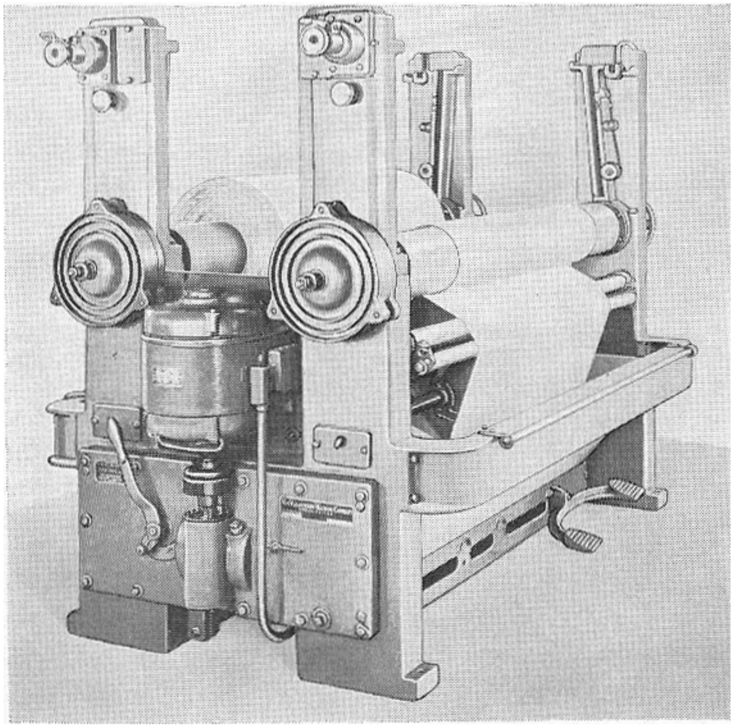
FIG. 2. TYPES OF PADDERS

The padder consists of two or three pairs of squeeze rolls mounted over a shallow pan containing the dye liquor and a guide roll. Both rolls in each pair are usually made of hard rubber, but on some models one roll is made of hard rubber and the other is made of stainless steel. Through a system of levers and weights, or by means of a hydraulic system, even pressure is maintained at all points along the rolls. The pressure may be regulated, depending on the type of fabric to be run, the amount of dye pickup desired, and similar factors.

20. Padder units may be set up in different ways. The three types used most often for dyeing are illustrated in Fig. 2, (*a*) to (*c*). In (*a*), slop, or nip, padding is shown. The lower part of the bottom squeeze roll *1* is immersed in the dye liquor *2*. The liquor adheres to this roll and is carried to the cloth *3*. The roll must be run at very high speeds in order to have enough dye liquor carried on the roller.

In (*b*) the use of the padder in immersion dyeing is shown. The cloth passes over the first guide roll *4* into the dye liquor, then under the second guide roll *5* out of the bath, and through the squeeze rolls. After that the material is rolled onto another roll and batched; or it passes continuously through the subsequent operations of washing, developing, and so forth.

A very small pad box, containing a highly concentrated dyestuff, is used in the padder shown in (*c*). The pickup, that is, the amount of liquor retained in the goods after passing through the squeeze, is high in relation to the amount of liquor in the bath. Consequently, a continuous feeding of dye liquor into the pan is necessary. This method offers the advantage of always having a relatively fresh supply of dye liquor in the box. It is particularly suitable where two or more dyestuffs are used in combination to obtain a given shade. However, one of the dyes may exhaust more readily than another, and this is likely to result in a



Courtesy of Van Vlaanderen Machine Company

FIG. 3. DYE JIG

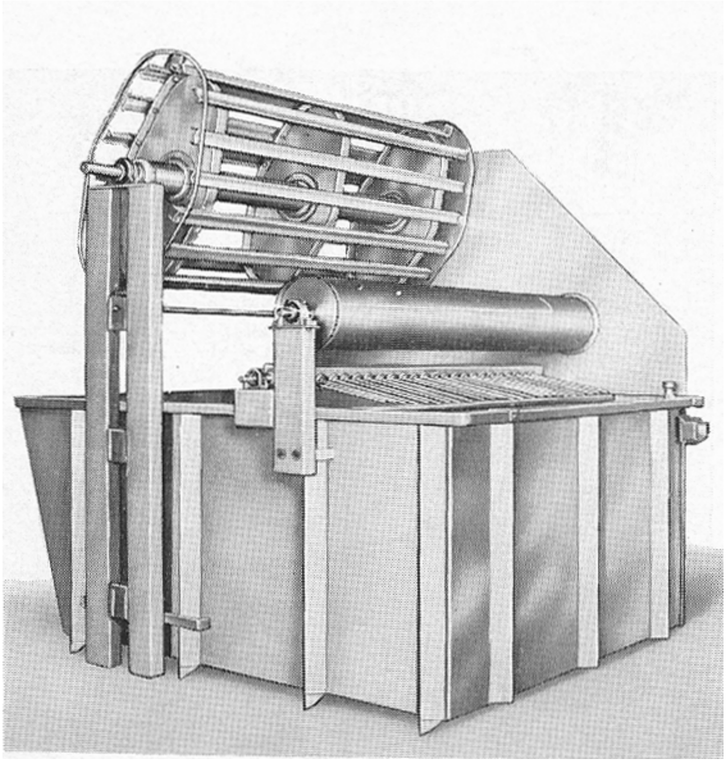
different shade near the end of a roll of goods than at the beginning, if the liquor is not changed rapidly.

The use of the padder is fast becoming the preferred method of applying most types of dyestuffs to cotton piece goods. Although padding still fails to give the best results when some of the other fibers are processed, more and more research into these fields is being done every day.

Dye Jig

21. Another type of machine, commonly known as a jig, is utilized for dyeing piece goods in open width. A jig is shown in Fig. 3. This machine has two batch rolls, one on either side of an immersion tank. The piece goods are passed from one batch roll to the other in open width through the bath, guided by two immersion guide rolls.

The tank of the jig is narrow and deep. The temperature can be controlled, either with live steam that goes directly into the dye liquor, or by the false-bottom and coil method. The immersion guide rolls are located near the bottom of the tank, so that a very low liquor level may be maintained if desired. There are also



Courtesy of Cadgene Machinery Company

FIG. 4. DYE BECK

guide rolls directly beneath the batch rolls, which work on a pendulum principle. These rolls serve to guide the material back to the batch rolls evenly.

22. The material is threaded through the jig by means of a leader cloth. It starts from the first batch roll, down between the first pair of guide rolls, into the bath, and under the two immersion guide rolls. It then leaves the bath, going through the second pair of guide rolls and onto the second batch roll. The leader cloth is usually waste material, about 10 or 15 ft (feet) long, sewn on both ends of the roll of cloth to be dyed. This enables the entire roll of goods to be dyed without having to thread the machine for each passage.

After the tank has been prepared for dyeing, the machine is started. When all the material has passed from one batch roll to the other, one cycle has been completed. The jig is then reversed and the cloth run back to the first roll. An even number of cycles is usually recommended, to prevent heavier dyeing at one end of the cloth than at the other. The process of reversing the machinery is continued until the desired shade is obtained. The dyeing is actually done on the batch rolls, where the dyestuff picked up during the immersion has a chance to fix or develop on the fibers.

The temperature is not, of course, as high on the rolls as in the bath; therefore, when the material requires an exceptionally high temperature in order to be dyed, this form of dyeing may not be practicable. However, devices have been applied to the jig whereby the batch rolls are covered to hold the steam in, so that the steam keeps the temperature fairly constant. With an arrangement of this nature, high-temperature dyeings may be done. Other developments include tensionless equipment with automatic reversing mechanism. The control of tension is particularly important in the dyeing of fine cotton fabrics and fabrics made from synthetic fibers.

Dye Beck

23. The reel, or winch, machine, commonly called the dye beck, is shown in Fig. 4. This machine is used for dyeing piece goods that are not subject to creasing when handled in the rope form. On top of the dye beck is a mechanically driven circular, elliptical, or triangular reel, or winch, mounted on a steel form and extending the full width of the dye box. In the front of the box is a perforated partition providing a space for steam pipes and for the addition of dye solution and chemicals. The reel, assisted by a guide roll at the front of the beck, lifts the cloth out of the bath. A guide bar with adjustable pegs keeps the individual strands of cloth separate, preventing entanglement.

In loading, the fabric is passed over the reel and through the machine. The ends are sewn together, forming an endless loop around the reel, guide roll, and guide bar. After the machine has been started, the material will fall into place between two of the pegs. Any number of individual loops may be formed on the machine, depending on the amount of work to be done, the bulk of the goods, and the width of the machine. The length of the loops may range from 10 to 100 yd (yards).

24. The reel of the dye beck may be threaded continuously to form one spiral loop coming in on one side of the width and leaving on the other. This is done where the material can be brought in rope form directly from the scouring bath and can be passed, after dyeing, directly into the finishing baths. But there are very few dye houses equipped to handle the material in this manner; the process is only mentioned as something of interest.

The loops, after passing over the reel, fall down the back of the machine in pleats, one on top of the other. The material remains in the bath until the reel, assisted by the guide roll, pulls the lowest pleat out from under the others. The material is then lowered down the back of the machine, and the cycle starts over again. This continues until the proper shade has been reached, after which the bath may be dropped and the next treatment carried out on the same machine. But if the liquor is to be saved, the material is removed and treated on other machines.

The reel is usually constructed of wood or stainless steel wrapped with cloth to prevent the material to be dyed from getting chafe marks. The tank is constructed of stainless steel, and so is the guide roll. The guide bar and pegs are either stainless steel or wood, also protected by cloth if the material is subject to chafe marks.

25. Among the developments for the dye beck are 1) automatic shutoffs in case of snarls, and 2) automatic temperature controls and total enclosure of the machine to maintain the temperature.

Another development of the reel-type dyeing machine is the Duplex machine. This machine is a combination of two reel machines in one. The reels revolve in opposite directions, bringing the cloth out of the liquor and immediately returning it, without excessive cooling. The tanks are in compartments, with a continuous threading from one tank to the other. The liquor in the tanks may be allowed to flow from one tank to the other, or the connections may be shut off, separating the two tanks. If the tanks are separated, the material can be washed and rinsed, or soaped and rinsed, alternately. During dyeing operations the material can be dyed, aftertreated or developed, rinsed, soaped, and rinsed again, all on the same machine. The speed, amount of liquor, temperature, and amount of material may be controlled easily to meet specific needs.

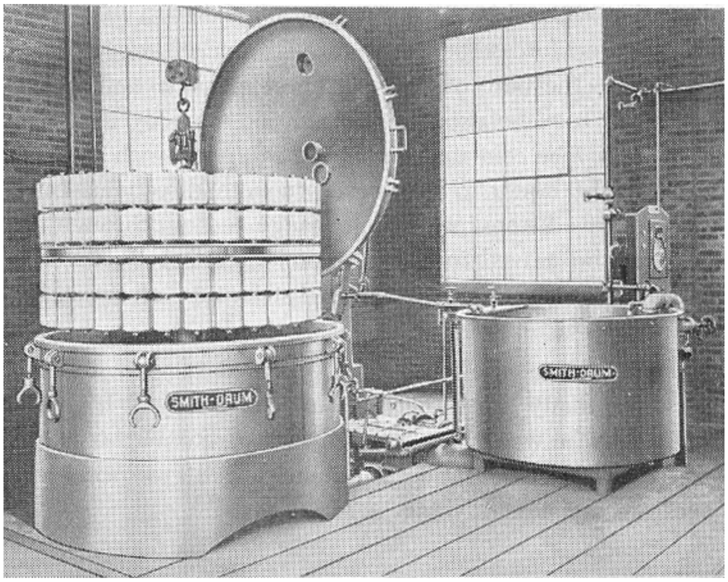
Continuous-Processing Machine

26. Characteristic of continuous-processing equipment is the DuPont Pad-Steam Process. This machine is designed to apply vat dyes continuously to cotton piece goods at high speeds and to obtain the best possible fastness and uniform shading of the dyed fabrics. The pad-steam range consists of a pigment padder, a hot-flue dryer or a set of dry cans, a chemical padder, a steamer, and several wash boxes followed by dry cans. The absorbent fabric picks up the vat pigment in the first padder, is squeezed and dried. It then enters the chemical padder and picks up caustic soda and hydrosulfite, which are necessary for the development of the dye. The fabric next goes into the steamer for twenty to sixty seconds at 214 F to 225 F, where the dye is reduced and fixed to the fiber. When the fabric emerges from the steamer, it is rinsed to remove the excess alkali and reducing agent, then oxidized with a chemical oxidizing agent, such as sodium bichromate and acetic acid, hydrogen peroxide, or sodium perborate. After this the fabric is rinsed in one box, soaped in the next two boxes, and finally rinsed and dried.

Stock-Dyeing Machines

27. The machines discussed thus far have been ones that operate on the principle of moving the material through the dye liquor. For stock-dyeing, however, a machine that circulates the liquor through the material is often used.

The stock-dyeing machine holds the material in a cylindrical basket which is perforated on the sides but has a solid bottom. The basket, which has a perforated spindle in the center, is also fitted with a lid. After the basket has been



Courtesy of Smith Drum & Company

FIG. 5. PACKAGE-DYEING MACHINE

filled with the material to be dyed, it is lowered mechanically into a solid cylinder. The spindle is then screwed down through the bottom of the basket and into the seat in the dye vat. The lid is then closed and made fast to the spindle. Thus the basket is also made fast to the bottom of the vat. A centrifugal pump is used to circulate the liquor from the vat through the material.

The stock-dyeing machine just described was one of the earliest types of machines designed to operate on the liquor-movement principle. It is used mostly for dyeing raw cotton and synthetic staple. In some exceptional cases yarn in skein form may be processed on this type of machine. There are on the market several models of stock-dyeing machines which differ in construction, but which operate more or less like the one described. Some of these machines have a separate expansion tank to hold the dye liquor. The tank is connected with the machine, and the liquor circulates from the tank through the machine.

Package-Dyeing Machines

28. Some dyeing machines, such as the one shown in Fig. 5, are designed to dye yarn in package form. The packages are made by winding the yarn around a perforated tube or spool until the yarn comes to a weight of 1 or 2 lb. The packages are packed in a container with vertical perforated spindles which fit inside the perforated yarn tubes. The upper rows of packages in some models are separated from the lower rows by means of a cylindrical manifold connected through the spindles. The container is then lowered into the vat, and the lid is

fastened on very tightly. Rubber gaskets make the machine watertight. This is very important, because when pressure is applied there must be no leakage.

A centrifugal pump forces the liquor through one of two pipes leading from an expansion tank to the base of the vat. The expansion tank contains the dye liquor, and the tank may be used to feed one or more dyeing chambers when connected in a series. The centrifugal pump is equipped with a reversing mechanism which allows the liquor to be worked in both directions. In other words, the liquor may be moved from inside the package and out through the perforated spindles, or it may be moved in the opposite direction. By reversing the flow every few minutes, an even and uniform distribution of dyestuff is obtained throughout the package.

Package machines are made to hold up to 1000 lb of yarn, and when they are connected in series, many times that amount can be dyed from the same dye liquor. The yarn may be wet out or scoured in separate machines before dyeing; but in most cases better penetration is obtained, and crossovers are prevented, if the packages are dry when dyeing begins.

Cascade Machines

29. One machine that is used for skein-dyeing is known as the cascade machine. This machine is constructed like the rotating-arm machine in two important respects: the dye box is the same, and the arms extend over the bath in the same manner. With the cascade machine, however, the skeins are not lowered into the liquor but remain hanging over the bath. The arms are perforated in this machine and are rotated mechanically. The dye liquor is pumped through the arms, or spindles, and onto the yarn in a continuous flow. The liquor flows through the perforations and soaks through the yarn on the arm. Material dyed in this manner is usually left in excellent condition, and therefore the method is used a great deal for the skein-dyeing of rayon and other sensitive yarns.

Hussong Machine

30. The Hussong dyeing machine consists of a rectangular box. Yarn skeins may be placed on racks, or raw stock may be dyed in perforated containers inserted in this box. At one end of the box is a well containing two reversible propellers on vertical shafts. The well is arranged with an opening at the top and bottom of the side of the box. This arrangement permits circulation of liquor downward through the material, then along the bottom of the box into the bottom of the well, out of the top of the well, along the top of the box above the load, and so forth, in a continuous cycle. The direction of flow can be reversed by reversing the propellers. When the flow is upward in the box, the skeins are lifted a little from the sticks on which they rest. Thus the liquor will reach the unexposed portions of the skeins that were in contact with the sticks. Stainless-steel linings in the box make the machine suitable for the application of any type of dyestuff.

Williams Unit

31. One machine used for the continuous dyeing or finishing of piece goods is known as the Williams unit. In this machine both the liquor and the material are moved at the same time. Actually, the liquor is set in motion when the material passes through narrow channels which contain the dye liquor. Both the cloth and the liquor enter the unit at one end and pass downward through half-inch channels. The cloth continues upward on the other side of the removable baffles, and on into another baffle-channel arrangement. The dye liquor flows out of drains at the bottom of each channel and returns to the main feeding tank.

The restricted volume of dye liquor permits an increase in the effective concentration of dyes or chemicals, because the liquor ratio is decreased. The temperature of the dye is controlled by steam chests. Several Williams units may be connected in series, allowing dyeing and developing to be done continuously. A padder is also incorporated into the unit. This may be used to apply dyestuffs or to squeeze out surplus fluids.

Direct, Sulfur, and Naphthol Dyes

Storage and Handling

32. Dyestuffs should not be stored in the dyehouse, but in a separate room. They should have a low, uniform temperature, and they must be protected from frost. It is also important that the humidity of the storeroom should not be very high, because dyes are likely to cake when damp. Powdered dyestuffs should be stored in tightly closed tins or barrels, in order to prevent absorption of moisture from the air. Sulfur dyes especially are sensitive to the prolonged influence of dampness and heat, and should always be protected from these conditions. When storing the leuco esters of vat dyestuffs, their extreme sensitivity to acid vapor and to light, particularly sunlight, must be borne in mind. Naphthols and the fast-color salts are also extremely sensitive to heat, moisture, and light.

Drying up of paste dyestuffs can be prevented by placing a moist cloth over the opening of the container before closing the lid. Many paste dyestuffs settle down more or less when left standing for a period of time. They should be well stirred in order to ensure an even distribution of the active dyestuff before taking out a quantity and weighing it for use.

Paste dyestuffs should always be protected from freezing, because freezing can easily result in an alteration of the dyestuff particles. Such alteration will cause uneven and faulty dyeings, as well as reduce the strength of the dyes considerably. If the paste types should accidentally become frozen, they should be thawed out very carefully and thoroughly. They must then be stirred well and strained through a sieve. Afterward they can be dissolved, but again great care must be exercised.

When dyestuffs have been in storage for a long period of time, they should be tested for loss of shade and strength before the percentages needed for dyeing are calculated. Where there is a considerable loss of shade and strength, the dyestuff should be discarded. The use of such a product may result in a heavy loss to the plant due to spoilage of large quantities of material.

Direct Dyes

33. Direct dyestuffs are those which exhaust on cellulosic fibers from a neutral or weakly alkaline salt bath. Because of this property, they are also called substantive dyes. Chemically, nearly all direct dyes are azo compounds, containing a sulfonic radical which makes them soluble in water. Some direct dyes possess excellent light fastness. Because they are so soluble and are held on the cellulosic fiber only loosely, they can be removed to a lesser or greater extent by hot soaping. In fact, many are so loosely bound that they will bleed in cold water or on contact with perspiration. However, in many cases, suitable chemical aftertreatment of the dyeing improves the wash fastness considerably. These treatments will be discussed later in the text.

The chemical structures of the direct dyes are listed in the Colour Index, a joint publication of the Society of Dyers and Colourists, a British association, and the American Association of Textile Chemists and Colorists. Dyes of the same chemical structures are grouped under a generic name, such as Direct Yellow 7, Acid Red 4, and so on, whether they are American-made or foreign-made.

34. Direct dyestuffs are used in dyeing cotton, rayon and cupra rayon, linen, wool, silk, ramie, hemp, jute, and some regenerated protein types of fibers. Acetate is stained by direct dyestuffs in many instances. A full and complete range of colors from the brightest blues to the dullest browns is easily obtained through combinations of one or more dyestuffs. The ease and simplicity of the dyeing procedure have caused the household packaged dyestuff manufacturers to choose combinations of direct dyestuffs. Garment dyers have shown the same preference, using direct dyes when readying or covering in their establishments.

The dyeings resulting from direct dyes are usually excellently penetrated, fully covered, and very even. The material does not lose its original luster or character. Though direct dyes will answer all medium-to-low requirements, the fastness properties are not alway as good as desired. When light fastness is desired, a dyer will select direct dyes which have excellent fastness to light but which may have poor fastness to washing. In other words, the dyer will select the dye having the desired fastness. Aftertreatments of the various types will usually improve the

TABLE 2

DIRECT DYES

Dyestuff	C. I. Name
	DIRECT
Solantine Yellow 4GL	Yellow 44
Diphenyl Fast Yellow RLSW	Yellow 50
Pyrazol Orange GH	Orange 1
Pontamine Fast Orange S	Orange 26
Erie Scarlet B	Red 37
Amanil Fast Scarlet 4BA	Red 24
Trisulfon Violet B	Violet 22
Pheno Blue 2B	Blue 6
Amanil Sky Blue FF	Blue 1
Fastusol Turquoise LG	Blue 86
Amanil Green LT	Green 1
Chloramine Green BC	Green 6
Pontamine Brown BT	Brown 31
Diphenyl Fast Brown BRL	Brown 95
Calcomine Fast Black F	Black 9
Chloramine Black EX	Black 38
Diazine Black OB	Black 80
Diazo Black BHSW	Blue 2

wet fastness, but sometimes at a sacrifice of light fastness. In general, direct dyes are not used for fabrics that require washing, unless the washing is done at very low temperatures.

Different dyestuff manufacturers have marketed direct dyestuffs under brand names that indicate those which are fast to light. Typical names are Calcodur (Calco), Chlorantine Fast (Ciba), Solantine (National), Solophenyl (Geigy), Superlitefast (Althouse), Fastusol (General), and Pontamine (Du Pont). Some characteristic direct dyes are listed in Table 2, together with their Colour Index generic names.

Application

35. Prior to the application of direct dyes, the material to be dyed should be scoured and freed of all foreign matter, either by boiling off or by kier boiling. In neither case is it necessary to dry the goods before they enter the dyebath. Where convenient, the preparation and the dyeing may be done on the same machine. Before dyeing, however, be sure that all caustic and acid chemicals have been rinsed out well.

The water for dyeing should be softened if it is hard. If this is not done, the solubility of the dyestuff will be impaired and faulty dyeings will result. The amount of liquor in the bath is determined by the size of the machine, and also by the depth of color desired. For dyeing heavy shades, a lower liquor ratio should be used than for dyeing light or medium shades. A correct ratio allows good exhaustion of the dye bath and even coverage of the material.

Direct dyestuffs are dissolved in water. The preferred method is to place the dyestuff in a small quantity of water. Live steam is used to heat and stir the mixture until the dye is completely in solution. The solution is then added to the dyebath. Adding the dyestuff directly to the dyebath would be undesirable because there is no practical way to determine whether or not the dye is completely in solution.

Dyeing Methods

36. In general, the clean, wet-out material is entered into the dyebath at 120 F to 150 F. At the same time the necessary, carefully dissolved dyestuff and dyeing assistants are let into the bath. The temperature is raised to the boil and dyeing continued for 45 min at the boil. The heat is then removed and dyeing continued for 15 min in the cooling bath; this period is known as steeping. The dyed material is finally rinsed in cold water, hydroextracted, and dried.

The quantities of dyestuff used in the dyeings depend on the particular shade and depth of dyeing required. The quantities of both dyestuff and dyeing assistants necessary are calculated as a percentage of the weight of the material being dyed. For example: 1% dyestuff per 100 lb of material means that 1 lb of dyestuff is required; 1% dyeing assistant per 100 lb material means that 1 lb of dyeing assistant is required; and 10% common salt per 100 lb material means that 10 lb of salt is required.

There are four common methods of applying direct dyestuffs. These are as follows: 1) *x*% dyestuff, 0.25% to 0.5% synthetic dyeing assistant, and 5% to 20% common salt or Glauber's salt (anhydrous sodium sulfate); 2) *x*% dyestuff, 0.25% to 0.5% synthetic dyeing assistant, 1% to 2% soda ash, and 5% to 20% common salt or Glauber's salt; 3) *x*% dyestuff, 0.25% to 0.5% synthetic dyeing assistant, 2% to 3% disodium phosphate, and 5% to 20% common salt or Glauber's salt; and 4) *x*% dyestuff, 0.25% to 0.5% synthetic dyeing assistant, 1% to 2% acetic acid (28% concentration), and 5% to 20% common salt or Glauber's salt.

Almost all direct dyestuffs may be applied according to method 1. The dyestuffs that can be applied with method 1 can also be applied with method 2. The function of the soda ash in method 2 is to increase the solubility, and also to act as a retardant in cases where a certain dyestuff is not sufficiently level dyeing. Soda ash also increases the brightness of some reds, and it increases the strength and brightness of some blacks. Method 3 is used for yellows where the brightness and solubility might be impaired by the hardness of the water. Method 4 is used for a few triphenylmethane types; it is generally not used in conjunction with the other types.

37. The synthetic dyeing assistant used in any method should be an excellent penetrating agent as well as a good leveling agent and scum-dispersing agent. There are many such products on the market today. The dyestuff manufacturer will usually advise what type to use in specific instances.

The amount of salt required is dependent upon the desired depth of the dyeing. Heavy blacks may very well need up to 40% common salt for a good exhaust. Light shades may require no salt at all. Because salt is cheaper than dyestuff, it is advisable to add an extra 5% salt to a bath, rather than to add more dye, if sample clippings show that the dyeing has not reached the desired strength.

Dyeing does not always start with a rapid increase of the temperature of the bath to the boil. When mercerized yarn is being dyed, or when pale shades are desired, it is better to increase the temperature very gradually and to continue the dyeing longer during the cooling-off period. On the other hand, when deep blacks are desired, it is advisable to start the bath at a very high temperature in order to get immediate and complete penetration. Otherwise the dyestuff will accumulate on the material and form a bronze shade. An additional rinse, immediately after dyeing in a salt bath, is good for deep blacks, to set the dye and thus prevent migration during the drying time.

Uses

38. Direct dyes are economical and simple to apply, but lack all-around fast-

ness properties. They are chosen for fabrics whose end use will permit the use of direct dyes. They are generally poor to washing, chlorine, and perspiration, and many are poor to light. However, there is a select group of direct dyes which have outstanding light fastness, and these are used for automotive fabrics, upholstery and drapery material, rayon carpets, and wherever light fastness is the main requirement.

Direct dyes of lower light fastness can be used for linings and other applications that can tolerate the poorer fastness. For improving fastness of direct dyes to wet treatments, such as water, washing, and perspiration, there are several possible treatments. These treatments will be explained in detail later in the text.

When combinations of dyes are needed to obtain a specific shade, dyes with the same rate of exhaust should be used wherever possible. Manufacturers' shade cards denote the exhaust rate as slow, medium, or rapid. The more rapid dyes may dye uneven, whereas the slow-exhausting dyes may not reach the desired depth of shade. However, primary importance should be given to the use of dyes from the same group in compound shades in order to better control the shade match.

Direct dyes can be applied in any type of dye machinery. The form of the material determines the type of machinery to be used.

Fixing Agents

39. Many of the direct dyestuffs may be aftertreated to improve their fastness properties. The aftertreatments directly follow the dyeing procedure. The treatments are usually performed on the same machinery as the dyeing, except when dyeing is done in a standing bath. The aftertreatment agents may consist of cationic fixing agents, formaldehyde, chromium salts, or copper salts, or aftertreatment may consist of coupling by diazotization, or diazonium compounds.

Synthetic cationic fixing agents are products marketed by individual manufacturers, and no specific formula can be given. Generally from 1% to 8% of the agent, based on the weight of the goods, is used, with similar variations in time and temperature. The agents may be used in conjunction with copper salts, and when carefully used, they tend to increase the light fastness as well as the wash fastness of the goods. Unfortunately, the fixing products in many instances decrease the original light fastness of the dyes, and are also likely to dull and redden the shades. Suggestions made by the manufacturers usually produce the best results. The action of the products is that of insolubilizing the anion-active dyestuff with a cation-active substance.

Formaldehyde

40. Certain types of direct dyestuffs may be aftertreated with formaldehyde and acetic acid. This treatment improves the fastness to bleeding and washing, with little effect on the light fastness or on the shade.

TABLE 3

DIRECT DYES AFTERTREATED WITH METALLIC SALTS

Dyestuff	C. I. Name	Aftertreatment
	DIRECT	
Chloramine Yellow RS	Yellow 19	Copper
Pontamine Fast Orange S	Orange 26	Chrome and copper
Direct Fast Red F	Red 1	Chromium fluoride
Erie Brilliant Violet B	Violet 9	Copper
Direct Blue RW	Blue 22	Copper
Erie Green MT	Green 6	Chromium fluoride
Chloramine Dark Green B	Green 1	Chromium fluoride
Pontamine Catechu G	Brown 25	Chrome and copper
Phenamine Chrome Brown B	Brown 27	Chrome and copper
Direct Brown MR	Brown 2	Chrome and copper
Direct Deep Black EAC Ex. Conc.	Black 38	Chrome and copper

The following method should be applied: The thoroughly rinsed dyeings are entered into a fresh bath containing 1% to 2% formaldehyde (40% concentration) and 1% to 2% acetic acid (28% concentration) or formaldehyde and 0.4% to 0.8% formic acid (85% concentration). Continue the aftertreatment for 20 to 30 min. at 140 F. Then rinse and soap lightly in a fresh bath with 1% neutral soap, or 0.25% synthetic detergent, for 10 min at 130 F. Finally rinse and contine with cloth finishing.

Some of the brand names used by different manufacturers for dyes that can be treated with formaldehyde and an acid are Calcoform, Benzoform, Formal, Erieform, Plutoform, Formanil, Formalide, and Nyaform.

Copper Salts

41. The group of dyestuffs that can be aftertreated with copper sulfate and acetic acid is larger than the group that can be treated with formaldehyde. Characteristic dyes of this type are shown in Table 3. In most cases a copper salt treatment results in an improvement in light fastness only; sometimes, however, the wash fastness is also increased.

The method by which the goods are treated with copper salts is as follows: Enter the thoroughly rinsed dyeings into a fresh bath containing 1% to 3% copper sulfate and 1% to 3% acetic acid (28% concentration). Aftertreat for 20 to 30 min at 160 F. Then rinse, soap lightly, and rinse again, just as after formaldehyde treatments.

Chromium Salts

42. Aftertreatment with sodium or potassium bichromate improves the wet

TABLE 4

DEVELOPED DYES

Dyestuff	C. I. Name	Developer
	DIRECT	
Diazine Fast Yellow 2G	Yellow 62	Z
Diazo Orange 2R	Orange 74	BN
Diazine Orange GR	Orange 73	BN
Diazamine Scarlet RPC	Red 209	BN
Diazine Red 7BL	Red 153	BN
Diazo Bordeaux 2BL	Red 127	BN
Diazine Violet BL	Violet 67	BN
Diazophenyl Blue BR	Blue 120A	BN
Diazo Black BHSW	Blue 2	MT or BN
Diazo Green 2GL	Green 41	Z
Diazophenyl Brilliant Green 3G	Green 38	Z
Pontamine Diazo Brown R	Brown 111	BN
Pontamine Diazo Green BL	Green 47	Z
Amanil Developed Fast Black V	Black 78	BN or MT
Amanil Toluylene Orange R	Orange 10	Diazonium compounds
Direct Black GX	Black 38	Diazonium compounds

fastness of the dyestuff. There are only a few dyes manufactured today that require this type of treatment.

The method of application is as follows: Enter the well-rinsed dyeings into a fresh bath containing 2% sodium or potassium bichromate and 2% acetic acid (28% concentration). Aftertreat for 20 to 30 min at 160 F to 200 F. Rinse, soap lightly, and rinse again, as previously described.

The following method, combining the copper and chromium salts, can be used for some dyestuffs shown in Table 3 to improve the wet and light fastness. Enter the well-rinsed material into a fresh bath containing 1% to 2% sodium or potassium bichromate, 1% to 2% copper sulfate, and 2% to 4% acetic acid (28% concentration). Aftertreat for 20 to 30 min at 140 F to 160 F. Rinse, soap, and rinse again, as previously described.

Brand names used are Benzo Chrome, Diphenyl Chrome, Direct Chrome, Niagara Chrome, and Viscoform.

Diazo Dyes

43. The diazo dyes are a group of direct dyestuffs. Diazo dyes possess a free amino group in their composition and may be diazotized after application on the fiber. The dyes are further developed with a phenol, a naphthol, or an amine. The resultant dyeings show a great increase in fastness to washing over other types of direct dyestuffs.

Diazotizing is done with sodium nitrite and with either sulfuric acid or hydrochloric acid. The diazotized dyestuff is developed, or coupled, on the fiber. Because the dyes are diazotized and developed, they are often called D & D dyes. The group has a wide range of shades, from the bright yellows to the deep blacks. Diazo dyes are very popular when it is desired to have good wash fastness and printing dischargeability, without an adverse effect on the light fastness. In Table 4 some diazo dyes with their developers are listed. The developers are listed to the right of the group of dyes with which they are used.

Application

44. The diazo dyes are applied to the material in the same manner as other direct dyestuffs. When the dyeing has been completed, the goods are then thoroughly rinsed with cold water.

The dyed and rinsed goods are then ready for diazotizing. They are entered into a cold-water bath prepared with 1.5% to 3% sodium nitrite and 3% to 5% sulfuric acid 168 deg (degrees) Twaddell, or 5% to 7% hydrochloric acid, 32 deg Twaddell. Diazotize cold for 20 to 30 min, rinse thoroughly, and develop immediately.

The developing bath is prepared with 0.5% to 3% developer, the exact amount depending on the type of developer used and the depth of shade desired. The developer to be used to produce the shade is designated by the manufacturer for each dyestuff, as is indicated for those listed in Table 4. The diazotized and rinsed goods are entered into a fresh bath of cold water prepared with 1% to 3% 2-naphthol (beta naphthol), or 0.5% to 2% Developer Z (1-methyl-3-phenyl-pyrazolone), or 0.5% to 2% Developer MT (m-toluylene-diamine). Develop for 20 to 30 min in a cold bath. Then rinse and soap at 120 F with neutral soap or synthetic detergent.

The developers must be carefully dissolved in the bath. When 2-naphthol is used, paste it with warm water and one-third as much caustic soda as developer. The paste is then added to the cold developing bath. Developer Z is dissolved in warm water and added to the cold developing bath. Developer MT is mixed with warm water and an equal amount of soda ash. The mixture is then added to the cold developing bath.

Brand names under which diazo dyestuffs are marketed are Diazo, Diazine, Diazamine, Diazophenyl, Dipyrazo, and Pontamine Diazo.

Aftertreatment with Diazonium Compounds

45. A limited number of direct dyestuffs may be coupled with a diazonium compound after they have been exhausted on the fiber. Two such dyes are listed in Table 4, though the process constitutes an aftertreament rather than developing. Coupling produces a marked increase in fastness properties over untreated diazo dyestuffs, without the use of a two-bath D & D process. However, the range

TABLE 5

RESIN-FAST DIRECT DYES

Dyestuff	C. I. Name
	DIRECT
Solophenyl Yellow 2GL	Yellow 39
Amanil Supra Red 6BLL	Red 79
Durofast Rubine 3BLL	Red 83
Solantine Brown 8RL	Brown 112
Atlantic Resin Fast Violet RL	Violet 46
Calcodur Blue 6GFL	Blue 76
Pyrazol Fast Blue RUL	Blue 80
Amanil Supra Blue LLG	Blue 98
Fastusol Gray LVGL	Black 71

of shades is not very great, consisting only of brown, olive, dark blue, and black. Only two developers are generally used.

The dyeing is carried out in the same manner as was described for direct dyestuffs, followed by a thorough rinse. The goods are then entered into a fresh bath prepared with 1% to 2% diazotized p-nitraniline, or 1% to 2% diazotized 2.5-dichloraniline, neutralized to Congo paper with a small amount of soda ash (about 0.5%) or with 0.25% sodium acetate. Couple for 30 min, cold. Then rinse and soap with neutral soap or synthetic detergent at 120 F to 160 F. Rinse again and continue the finishing. The diazotized developers are produced in the stable compound form, requiring only cold water to put them into solution.

Resin Treatment

46. Many woven materials of cotton or rayon, as well as blends and mixed-fiber fabrics containing cotton or rayon, are given a resin finish to provide hand and shrinkage control, or simply to build the weight of the fabric. Some of these resins, particularly urea-formaldehyde and melamine-formaldehyde resins, improve the fastness of direct color dyeings to such washing and wet treatments as cold water bleed and perspiration. It has been found, however, that this advantage may carry with it a serious disadvantage, in that the light fastness of the dyeing is sometimes degraded. The loss in light fastness is often greatest for dyes which have high light fastness before resin treatment.

Many direct dyestuffs have high light fastness and retain a large measure of that fastness after resin treatment. A listing of such characteristic direct dyes is given in Table 5. Addition of small amounts of copper salts, such as cuprous chloride, to the resin-impregnating bath helps restore the loss in light fastness in many cases. However, copper salts have a tendency to dull the shades.

Sulfur Dyes

47. The sulfur dyestuffs belong to the group of substantive cotton dyes. They

TABLE 6

SULFUR DYES

Dyestuff	C. I. Name
	SULFUR
Sulfur Yellow RCF	Yellow 2
Katigen Yellow BG Ex.	Yellow 4
Sodyesul Liquid Brown 5RCF	Red 5
Sulfur Bordeaux BCF	Red 6
Calcogene Blue 6RCF	Blue 7
Sulfindone Brilliant Blue 8GCF	Blue 15
Sodyesul Green NCF	Green 2
Sulfur Green 3G	Green 3
Sulfogene Brilliant Green J	Green 14
Sulfur Brown CGCF	Brown 10
Katigen Brown W	Brown 14
Sodyesul Liquid Black 4GCF	Black 1
Sulfogene Carbon 4RCF	Black 2
Indo Carbon CLGS	Black 6

are called sulfur dyes because they consist of sulfur compounds, and they are generally used with the addition of sodium sulfide to the dye bath.

Sulfur dyes are particularly noted for their relatively fast and strong colors. They possess much better wet fastness than direct dyes. In light fastness they are equal to, or somewhat better than, the fast-to-light direct dyes or the copper-aftertreated direct dyes, particularly if they are applied in dark shades. They are generally inferior to the vat and naphthol dyes in fastness properties.

Characteristic sulfur dyes are listed in Table 6. The shade range of sulfur dyes is not as complete as that of some other groups. There are no red shades in sulfur dyes, but there are excellent heavy shades of brown, tan, blue, and black. The sulfur yellows, oranges, blues, greens, and violets lack the brightness that direct dyestuffs have.

Preparatory Processes

48. In preparing the material for dyeing with sulfur dyes, the same general precautions should be taken as are taken with direct dyes. However, some types of goods may be dyed without first scouring the material. This is particularly true when heavy shades are to be dyed on fairly clean material. When this is the case, a simple wetting-out prior to dyeing may be sufficient.

Sulfur dyes are not soluble in water. They possess practically no affinity for textiles, unless the dyes are made soluble. Sulfur dyes become soluble when they are treated with a reducing agent to form a reduced, or leuco, compound of the dyestuff. These reduced, water-soluble compounds possess considerable affinity for cellulosic fibers. The dyestuffs are best dissolved by alkaline reducing agents.

Sodium sulfide is commonly used because it is quite suitable and is low in price. An alkali, such as soda ash, should also be used in the process for best results.

Sulfur dyestuffs are generally dissolved in wooden, stainless-steel, or porcelain-lined vessels, because these vessels are not attacked by the sodium sulfide. The dyestuff is made into a paste with a small amount of cold water and synthetic dispersing agent. The required amounts of sodium sulfide chips, soda ash, and water are added, and the whole mixture is boiled for 10 min. Products which have a dyeing temperature of 140 F to 180 F are dissolved at their respective dyeing temperatures.

The amount of sodium sulfide that must be used depends upon the kind of dyestuff, the depth of shade desired, the amount of dye liquor, and the type of machine used for dyeing. The amount of soda ash required varies from 1% to 5%, the exact amount depending on the factors just mentioned.

Application

49. The dissolved sulfur dyestuff is usually applied from a hot alkaline bath. The clean wet-out cotton is entered into the dye bath at 140 F to 200 F and run from 45 min to 1 hr. Common salt or Glauber's salt is added 15 to 20 min after the material is entered into the dye bath, in order to aid the exhaustion of the bath. The amounts of salt necessary for the exhaustion of the dye bath depend upon the dye used, the depth of shade to be produced, the kind of material to be dyed, and the type of machinery employed. Generally, the same amounts of salt are used for sulfur dyestuffs as are used for direct dyestuffs.

During the dyeing operation it is important that the material be kept well covered, or well saturated, with the dye liquor. If portions of the dyeings are exposed to air during the dyeing time, uneven and spotty dyeing will result. After dyeing, the dyestuff on the material must be oxidized to convert the product back to the insoluble, or oxidized, state. Prior to oxidation, the material is rinsed in cold water. After rinsing, the material may be hung in the air to oxidize, or treaetd with a suitable oxidizing agent. Oxidation fixes the dye. It also develops the correct shade and properties of sulfur dyes.

50. The shade and fastness properties of sulfur-dyed fabrics can be controlled to a great extent by the choice of the oxidizing agents, as well as by various after-treatments. Sodium or potassium bichromate and acetic acid are the most commonly used chemicals for oxidizing. If maximum light fastness is desired, copper sulfate and acetic acid may be employed, either alone or in combination with the bichromate. The treatment is carried out in a fresh bath at 140 F to 180 F for 20 to 30 min. The following quantities of chemicals are employed: 1% to 3% sodium or potassium bichromate, 1% to 3% copper sulfate, and 1% to 5% acetic acid (28% concentration). These quantities vary, depending on the depth of shade and the effect desired. The oxidation is followed by rinsing, soaping, and

rinsing again. This will remove any unfixed dyestuff and chemicals which might hurt the shade or the fastness properties of the finished dyeings.

Use of Sulfur Dyes

51. Sulfur dyes may be used to dye cotton in the form of raw stock, sliver, and yarn, as well as in the form of piece goods. Dye jigs and continuous dyeing machines are used. Sulfur dyes are very seldom used for silk and rayon, because the hand of these goods deteriorates. The low cost, and the good fastness properties to light and water, give sulfur dyes an important place in the dyeing of work clothes, socks, cotton duck, and backing for wool and mohair pile fabrics.

A slight tendering effect on the fiber may result from storage in a warm, moist atmosphere. Under these conditions the dyestuff itself begins to oxidize, forming sulfuric and sulfonic acid. This danger may be prevented by leaving a trace of soda ash, sodium acetate, soap, or some other buffering salts in the goods after the last rinse. In ordinary use, where the material is laundered frequently, this problem will not arise.

Brand names under which manufacturers market sulfur dyes are Sulfogene, Immedial, Acco Sulfur, Amalthion, Indo Carbon, Pyrogen, Calcogene, Sulfur, Katigen, So-Dye-Sul, Sulfindone, and Thional. The manufacturers' color cards and literature describe the recommended amounts of dissolving chemicals, the temperature at which the material is to be dyed, and the proper aftertreatment to be used for each individual type of dyestuff.

Naphthol Dyes

52. The naphthol dyes are insoluble azo dyestuffs. They are produced on and in the fiber by combining with fast-color salts, or with diazotized fast-color bases. Naphthol dyes have been widely adopted to produce dyeings that are fast to washing, chlorine, and light. These dyes are mostly used on cellulosic fibers, but they can also be used on silk, wool, and synthetic protein fibers.

The discovery of dyeing by the naphthol process came about in 1880 when Read Holliday & Sons found that a fast red shade could be obtained by coupling 2-naphthol with a solution of diazotized 2-naphthylamine. The resultant shade, called Vacanceine Red, was cheaper and easier to produce than a Turkey red using alizarin. In 1912 Chemische Fabrik Griesheim-Elektron introduced Naphthol AS, which is the anilide of 3-hydroxy-2-naphthoic acid. This product was the basis for all of the future developments in the naphthol field. The dyeings that resulted when Naphthol AS and a solution of diazotized p-nitroaniline were coupled were excellent. They were so much faster to rubbing and sublimation that all types of dyes previously used for the purpose were discontinued. The number of different naphthols continued to grow at a rapid rate, and so did the fast organic bases. Today there are over three dozen naphthols and some fifty bases. The range of shades has expanded from the original red shade to almost any shade desired.

TABLE 7

SUBSTANTIVITY OF NAPHTHOLS

Naphthol	Substantivity Without Salt	Substantivity With 15% Common Salt
AS	10	14
AS-D	10	14
AS-G	10	20
AS-PH	13	23
AS-OL	13	23
AS-RL	16	27
AS-BG	16	27
AS-TR	18	30
AS-ITR	18	30
AS-KB	18	30
AS-BS	18	30
AS-EL	18	30
AS-MX	18	30
AS-BO	22	32
AS-E	25	40
AS-SW	35	54
AS-BR	40	—
AS-LG	45	62
AS-LB	45	62
AS-DB	45	62
AS-SG	93	—
AS-SR	93	—
AS-GR	75	92

Preparation for Dyeing

53. The dyeing operation really consists of two operations: 1) impregnation of the material with the naphthol solution; and 2) developing, or coupling, the impregnated naphthol with a solution of a fast-color salt, or with a diazotized fast-color base. Because there are on the market about forty different naphthols, or azoic coupling components as they are called, and about fifty fast-color salts or bases, 2000 shade combinations are possible. Since naphthols may be mixed together, an endless number of shades can be produced. However, not all of these combinations possess satisfactory fastness to washing, sublimation, and light. The manufacturers usually produce shade cards or literature indicating the specific combinations that will produce a color with reasonable fastness.

Prior to naphthol dyeing, cotton in the form of raw stock or yarn should be thoroughly boiled off with a detergent and an alkali to remove as much of the natural impurities in the material as is possible. Piece goods should be completely absorbent for padding. If the piece goods are to be dyed on a jig, the boil-off may be done on the jig prior to naphtholating.

Selection of Naphthols

54. Naphthols may be applied on any type of dyeing machinery. The choice of the naphthol to be used on any particular machine depends a great deal on the substantivity of the naphthol itself. Naphthols with low substantivity are best applied on padders or other equipment which uses a comparatively small amount of dye liquor. The naphthols with medium-to-high substantivity may be used in machines employing a large amount of liquor.

The substantivity is the amount of naphthol which will actually exhaust onto the fiber. This amount may range from 10% to 95%, depending on the particular naphthol. The substantivity is also affected by the temperature in dyeing, and on the amount of salt in the dye bath. Table 7 shows the substantivity of twenty-three important naphthols when applied in 1-to-20 cloth-to-liquor ratio, both with and without the addition of salt.

The low-substantive naphthols, with substantivities up to 20%, exhibit poor affinity, and should be applied by impregnation on the padder. The higher substantive types may be applied in package-dyeing machines, on jigs, in skein-dyeing equipment, and even on the beck.

Dissolving the Naphthols

55. The various standard naphthol powders are water-insoluble compounds which must be brought into solution or dissolved before they can be used. Naphthols are converted into water-soluble materials by treatment with the strongly alkaline sodium hydroxide or caustic soda. An excess of caustic soda is necessary during the application or naphtholation process in order to keep the naphthol in solution and active for future development. For this reason, additional caustic soda is added to the application or naphtholating bath before the dissolved naphthol is put in.

There are two major methods used for dissolving naphthols, the cold-dissolving method and the hot-dissolving method. The cold-dissolving method is used where concentrated solutions are to be prepared. It is quick, and with this method smaller containers without external heating equipment can be used. The cold method consists in dissolving the naphthol with alcohol and caustic soda solution. This concentrated solution is added to the dyebath which has been sharpened with caustic soda.

The naphthol is then pasted up with denatured alcohol. Enough alcohol is used to form a thin slurry. At least two pints of alcohol is suggested for each pound of naphthol. For each pound of naphthol, 4 oz of caustic soda is dissolved in $\frac{1}{2}$ gal (gallon) of cold water. This solution is then added slowly, to the alcohol slurry, as the slurry is stirred. The caustic is added until a clear yellow solution is formed. Any caustic left over is added to the dye machine. If a clear solution does not form with all of the caustic solution added, more caustic soda must be dissolved and added. Best results are achieved if the caustic solution is hot when used. When the caustic is dissolved in cold water, the solution becomes hot, so that no heating is required if the solution is used immediately. Care must be taken while adding the caustic. An excess can cause the naphtholate to precipitate.

The dye liquor or pad solution to which the dissolved naphthol is to be added must be set with caustic soda before the naphthol is run in. In dyeing operations, the machine is spiked with at least 2 lb of caustic soda per 100 gal. Medium shades (1% dyeings) and heavy shades (2% dyeings and up) require 3 to 4 lb of caustic per 100 gal. In padding application, the pad liquor should contain a total of at least 1½ oz of caustic soda per gallon. For long runs on continuous ranges, high concentrations of caustic (2 to 2½ oz) per gallon have been found advantageous.

Some naphthols dissolve better with Cellosolve or diethylene glycol than with alcohol. Included in this group are the following:

Naphthols AS-SG
AS-SR
AS-BS

Naphthols AS-ITR
AS-TR

A minimum quantity of caustic should be used in dissolving naphthol yellows (AS-LG, AS-G, AS-L4G). Excess caustic reduces the maximum color yield.

56. In one hot-dissolving method, the naphthol is pasted with an equal volume of water, and with a dispersing agent. Hot water is added, and a mixed solution is obtained by adding a concentrated caustic soda solution and boiling the mixture until the solution is clear.

Since it is a representative type of naphthol, we will use Naphthol AS-SW as an example. The detailed formula is as follows: Paste 1 lb of Naphthol AS-SW with 5 pt (pints) of Eunaphthol AS or sulfonated castor oil (48% concentration), and 6 gal of hot water. Add 13.25 oz of dry caustic soda, 8 gal of cold water, and 0.5 pt of formaldehyde. The stabilizing time at the boil is 5 min. Sharpen, or prime, the dyebath with 0.5 pt of formaldehyde and 1 to 3 lb of dry caustic soda. Then add the boiled naphthol mixture to the dyebath.

Note that, according to the first sentence of this article, equal volumes of naphthol and water were to be used in pasting, yet 1 lb of Naphthol AS-SW and 6 gal of water are listed in the formula. The explanation is that the naphthols are very light in specific weight, and therefore take up a very large volume. Thus 1 lb of Naphthol AS-SW takes up as much space as 6 gal of water.

57. The other hot-dissolving method is known as the Supra method. The Naphthol Supra brands are first pasted with cold water and then further diluted with hot water. Caustic soda is added, and the mixture is boiled until a clear solution is obtained. The amount of dry caustic soda required varies from 40%

to 80% of the weight of the naphthol. The resultant solution may be used for padding, with no further addition of caustic. If the solution is to be used for other types of dyeing, the bath should be primed so that the final amount of caustic present is 1 lb per 100 gal of liquor for light shades and 3 lb per 100 gal of liquor for heavy shades.

A representative type of naphthol used for this dissolving method is Naphthol AS Supra. For each pound of Naphthol AS Supra, dissolved in 5 gal of water, use 6.5 oz of dry caustic soda. The water is kept hot, and the material is stabilized until a clear solution is formed. This solution can be used for high-speed padding, or it can be further diluted with a primed bath for other types of dyeing.

The sample formulas given do not apply to all naphthols. For each formula you should consult the manufacturer's recommendations. Among the variables encountered are the amounts of water to be used and the amounts of caustic and solvent needed; also variable are the type of pasting solvent and the possible need for the addition of formaldehyde.

Use of Formaldehyde

58. To increase the stability of the naphthol solution and improve the resistance of the impregnated material to air, formaldehyde can be added to the naphtholating bath.

If the material is to be dried immediately after impregnation, as in pad dyeing, no formaldehyde should be used. This is especially true if the cotton cloth is dried at temperatures over 170 F, or if the dyed cloth is to be discharge printed, because impregnations containing formaldehyde are more difficult to wash out of the discharge pattern.

Naphthol baths are relatively stable, but if a naphthol bath is to be used at a later time, or if the impregnated cloth must be exposed to the air, as during centrifuging, an addition of formaldehyde is recommended in the naphthol bath. The amount of formaldehyde to be added is, in general, an amount equal in weight to the naphthol itself. No formaldehyde should be used with Naphthols AS-G or AS-L4G.

Higher temperatures cause precipitation of naphthol solutions which contain formaldehyde. If formaldehyde is omitted, padding can be carried out as high as 180 F, whereby better penetration is obtained.

Preparing the Naphtholating Bath

59. There are six factors that must be considered in preparing the naphtholating bath. One of these factors is *the condition of the water.* To obtain the best results the water should be reasonably soft. Excessive hardness of the water may cause turbidity and flocculation. The lime salts and iron salts present in hard water will decrease the affinity of the naphtholate for the material. These impurities will combine with the naphtholate and render the solution much weaker than it originally was, and much below the proper strength. The use of a se-

questering agent made of the soluble sodium salt of ethylene diamine tetra acetic acid, commercially available under such names as Versene and Nullapon, will usually overcome any difficulties of this kind.

A second factor is *the concentration of the naphtholate.* A better exhaust is obtained when dyeing in a concentration intended to give weaker shades than when dyeing in a concentrated liquor. Consequently, percentagewise, less naphthol is actually needed when dyeing weaker shades.

A third factor is *the liquor ratio.* In a short liquor ratio, better use is made of the naphthol present than in longer liquors; hence less naphthol is required for heavy shades.

60. A fourth and important factor in naphthol dyeing is *the temperature of the bath.* In dyeing with naphthol it is well to remember that the lower the temperature, the more affinity the naphthol has for the material. The most favorable temperature is 85 F, except for Naphthol AS-BR, which has a maximum exhaust at 120 F. In order to have a better penetration and an even exhaust, it is sometimes advisable to start dyeing with a bath around 120 F, gradually cooling the bath while running the dye lot. In padding naphthols, the liquor is kept around 200 F. With this temperature the exhaust is slow, and thorough penetration of the material is achieved.

Still another factor to be considered is *the duration of impregnation.* The length of time it takes to impregnate the goods is about 30 min. After this time there is an equilibrium between the naphthol on the material and the naphthol remaining in the bath.

Finally, there may be *an addition of salt.* Salt may be added to the naphtholating bath to increase the absorption of the naphthol on the material. The salt may be either Glauber's salt or common salt. Recommended amounts of salt are: for low-substantive naphthols, additions of 5 oz per gal; for naphthols of medium substantivity, 2 oz per gal; and for high-substantive types, 1 oz per gal. For extremely high substantive types an addition of salt is not required. An excessive amount of salt is likely to precipitate the naphtholate, thus impairing the fastness to rubbing. The additions are made from a concentrated solution about 15 min after the dyeing has begun.

61. Solutions of naphthols are unstable and some become turbid on standing. When the dyebath is in use, the naphthol solution is constantly being exhausted and is therefore not apt to deteriorate. To increase the stability of the naphthol solution, a small amount of a sequestering agent, such as Sequestrene or Amaquest, is recommended.

Impregnated cloth is immediately sensitive to light, air, and acid fumes. Padded and dried cloth which is not coupled with the fast-color salt or base should be stored in a cool, dark room. Goods padded with solutions to which formaldehyde has been added are less sensitive to the atmosphere.

If a dye bath shows precipitation, it should be discarded at once. Most of the wetting agents and penetrating agents on the market will cause precipitation of the naphthol. Caution should be taken not to add wetting agents or penetrating agents to the naphthol solution until tests have been made to determine its campatibility.

Naphthol Dyeing Procedure

62. Naphthol dyeing may be carried out on any type of dyeing machinery. It may be done on material in the form of raw stock, sliver, chain warps, yarn in skeins or packages, and piece goods. Raw stock, sliver, and warp chains are usually impregnated in circulating liquor in open or closed machines. The material-to-liquor ratio in these machines may vary from a ratio of 1 to 2.5 to a ratio of 1 to 10, the ratio depending on the type and construction of machine used. Low-substantive naphthols may be used if the liquor is extracted from the material before coupling. Medium- to high-substantive naphthols may always be used to good advantage, as they can be salt-rinsed instead of being hydroextracted. Skeins may be dyed by hand in open boxes, on machines of the Klauder-Weldon type, on rotating-arm machines, or on cascade machines. In these machines the liquor ratio is 1 to 20 and naphthols with good substantivity should be used for the best results.

Yarn in the package form should be dyed in a closed pressure machine sucn as the Franklin or the Smith-Drum package machine. Naphthols of good fixation that can be salt rinsed should be the only types used on these machines.

Chain warps are usually impregnated on the continuous system. Naphthols having low substantivity produce best uniformity, with readily controllable results.

63. Piece goods can be naphtholated on the jig, padder, or continuous Williams unit type of machine. High-speed padding of the material with naphthols of low substantivity is the preferred method. However, all naphthols may be applied by the use of nip padding if the danger of two-sidedness is overcome. Two-sidedness can be overcome by using a spray arrangement against the upper roll, so that a well of liquor forms in front of the nip. In nip padding, the danger of tapering of shade due to exhaustion is reduced to a minimum. However, heavier types of piece goods are not easily penetrated with the use of a spray arrangement, and they should therefore be submerged in the pad liquor prior to squeezing. After padding, the naphtholated goods are dried before entering a developing bath. When dyeing with Williams units is continuous, a dryer is installed between the pad and the developing units.

Only those naphthols of good substantivity should be used for naphtholating piece goods on the jig. After the goods are naphtholated, they should be salt-rinsed prior to coupling. The salt rinse removes the excess alkalinity but retains the naphthol on the fabric.

Time and Temperature

64. The length of the naphtholating time varies according to the machines used. In padders, a short dip is used and a speed of 30 to 120 yd per min is maintained. The time for tub and reel dyeing is 30 min. On the package machine and the jig 45 min is the normal time, but heavy material on the jig may require 60 min.

The naphtholating temperature for tub, reel, and jig dyeing is 85 F. On the package machines, temperatures of 105 F to 115 F are used. Temperatures on the padder range from 120 F to boiling.

Intermediate Treatments

65. The intermediate treatments given to the naphtholated goods before coupling are 1) extraction, 2) salt rinsing, and 3) drying. For low-substantive naphthols, it is important that the material be very well extracted, so that no excess pigment will be formed during coupling. Excess pigment will cause poor fastness to rubbing and washing. Naphthols with higher substantivity may be salt rinsed in a solution made with 4 oz of salt per gallon of soft water.

When the material is to be dried before entering the coupling bath, care must be taken to avoid migration of the naphtholate during drying. This can best be accomplished by the hot-air system. With this system, the entire area of the fabric has an equal amount of hot air circulating about it at the same time. This method also prevents two-sidedness. Precautions must be taken when the material is dried over cans. The first few cans should be covered with cloth and the steam pressure should be kept low. Five pounds of steam pressure in the first set of cans, and 10 lb of steam pressure in the second set, should be satisfactory. Care should especially be taken if the material is dried on a frame. When a frame is used, the heat should be evenly distributed; otherwise, the naphthol will have the tendency to migrate from the wetter areas to the drier areas. The addition of 12 lb of salt for each 100 gal of naphtholating liquor will minimize this tendency to migrate.

The material which has been extracted or salt rinsed should be developed as soon as possible. The material which has been dried may be stored a short while and then developed. During storage, the dried naphtholated material should be protected against direct sunlight, against chlorine and acid fumes, and against water spotting. This is easily done by wrapping the material. The material should not be stored too long, because a certain amount of deterioration may take place, which will result in imperfect dyeings.

Developing

66. After the intermediate treatments have been accomplished, the next step toward the completion of a naphthol dyeing is the developing, or coupling. This step is accomplished by passing the material through a coupling bath. The liquor in the bath consists of a solution of a fast-color salt, or a solution of a diazotized fast-color base. Coupling continues until all of the naphtholate has combined with

the developer. The salts used for the coupling bath dissolve rather easily, compared to the bases. Consequently, most manufacturers are now marketing the stable diazotized form or salt of the bases. The bases, however, are much more economical than the salts. When sizable runs are to be made, it will often be to the advantage of the mill to use bases because of their economy.

Dissolving the Salts

67. The amount of fast-color salt required for coupling depends on the actual amount of naphtol fixed on the fiber. This amount can be determined by the substantivity of the dye, or by the method of application. Generally speaking, four times as much salt as the weight of the fixed naphthol is required. The amount of naphthol fixed is usually given by the dyestuff manufacturer.

Fast-color salts are dissolved by first pasting them with a small quantity of lukewarm water, diluting the paste immediately with cold water, and stirring the mixture until a complete solution is obtained. The mixed solution is then added to the developing bath. Heat should not be applied to the fast-color salt in solution at any time, because it may effect a decomposition of the material.

68. A number of the fast-color salts require the addition of sodium acetate or acetic acid in order to obtain a good coupling action. The coupling energy of the fast-color salts varies, and the speed of coupling can be largely controlled by the *p*H value, or hydrogen ion concentration. In general, the coupling energy and strength of the completed dyeing is reduced by acid additions, because most of the bases possess the strongest coupling action at a neutral *p*H. On the other hand, the diazo compounds are sensitive to caustic alkali, and must be protected from the alkali contained in the naphtholated material with weak acids, or with weakly acid alkali binding agents.

The fast-color salts which possess strong coupling energy should be handled in a bath that shows a strong acid reaction to litmus paper. In such a bath the stability of the diazo compound is assured. Fast-color salts which are sensitive to acid are handled in a bath containing 0.5 oz to 1 oz of sodium acetate per gallon of liquor; the bath also contains a small amount of acetic acid. By the use of this bath a buffered *p*H, lower than 5, is obtained, giving a solution that even the acid-sensitive fast-color salts can couple. Certain fast-color salts, which show a slow coupling speed even with this low *p*H, must be buffered with magnesium or zinc sulfate. If the acidity is still too high when using these chemicals, the diazo solution should be further buffered with sodium bicarbonate. Usually the sodium bicarbonate required is twice as much as the sodium nitrite used for diazotizing.

When wet-naphtholated goods are developed, it is sometimes advisable to add 10 to 20 lb of common salt to each 100 gal of solution in the developing bath. This addition will prevent the naphthol from loosening from the material.

The speeds at which the fast-color salts couple, and also the amounts and types of acid or alkali binding agents that are to be used, are specified for the dyer by the dyestuff manufacturers. After the developing bath has been properly prepared, the naphtholated goods are immersed in the liquor and run for a length of time equal to that spent in the naphtholating bath. The same type of machinery is used, except that the padder is not practical for coupling. If the goods have been naphtholated by padding, they are usually developed either on the jig in full width, or on a reel in semiopen width. When Williams units are available, these may be used for developing.

Special Process

69. For certain blues, blacks, and violets it is necessary to use a special process which gives a better control over the final shade. This process, called the acetic acid–caustic soda process, employs approximately 10% excess caustic in the pad liquor. After the material has been run through the padder, it is skied; that is, it is exposed to light and open air, in this case for 30 sec (seconds). Then the material is once more passed through the padder at 50 F. The padder contains the dissolved salt, plus the required amount of acetic acid. The material is skied again, and then run through a vat roller containing 1.5 oz of soda ash per gallon of liquor at 85 F. Finally, the material is aftertreated in the usual manner.

Dissolving the Bases

70. The fast-color bases are inconvenient to dissolve, but they are usually more economical than the salts. They require a diazotizing procedure involving the use of sodium nitrite and hydrochloric acid. Each base has its own specific method for diazotizing, which can be learned from the dyestuff manufacturers.

In order to give you a general idea of what the procedure involves, we will use as an example the diazotizing formula for Fast Red GG base. First, 2.2 lb of Fast Red GG base is pasted up well with 1.4 qt (quarts) of hot water. To the paste, 1.2 lb of sodium nitrite is added. After the nitrite is completely dissolved, the paste is cooled and quickly stirred into a mixture of 4.5 gal of cold water and 2 qt of hydrochloric acid at 32 deg Twaddell. A little ice may be added to keep this mixture cold. The mixture is stirred until the paste is completely dissolved. The solution is then filtered and neutralized with 2.4 lb of sodium acetate, dissolved in 2 qt of water. Finally, 0.6 qt of acetic acid (50% concentration) is added.

The diazotizing temperature is about 50 F. The diazotized base solution is filtered and entered into the dyebath. Subsequently, the dyebath is brought up to the required volume, and the procedure is continued in the manner outlined for salt solutions.

Aftertreatment

71. Immediately after coupling, the material should be rinsed several times in cold water to remove any excess color lake that may have formed on the goods. The material is then soaped at the boil for 30 min, in a bath containing 3 lb of soap and 2 lb of soda ash per 100 gal of water. There are certain exceptions to the

use of boiling, which are listed by the manufacturers. The addition of an organic sequestering agent is recommended for hard-water areas. This increases the brightness of the shades, and at the same time preserves the increase in wash, light, rubbing, and chlorine fastness which results from careful aftertreatment.

For some blues, the light fastness may be improved by aftertreating for 30 min at the boil in a solution containing 1.5 lb of copper sulfate and 1.5 lb of acetic acid (56% concentration) per 100 gal of liquor. The usual soaping is not necessary, because the fastness to crocking, or rubbing off, is also increased by this treatment.

Storage of Chemicals

72. The storage stability of fast-color salts is not good. They should be kept in a cool, dry place, and checked for strength at regular intervals. The storage life of some of the salts is less than 6 months. If they are allowed to deteriorate, inferior dyeings will result. The bases and the naphthols are considerably more stable than the salts, but they should be protected from the effect of acid fumes and light.

Package Dyeing

73. It often happens that a lot of packaged yarn is to be dyed in two or three portions. In such cases it is sometimes advantageous to dye from a standing bath. This method allows a considerable saving in chemical and dye costs. With a little practice, uniform results are easily obtainable.

For example, let us assume that 1200 lb of 2/40s cotton yarn is to be dyed in two 300-lb-capacity Smith-Drum package-dyeing machines with a 500-gal volume. The yarn is to be dyed with 2.3% Naphthol AS-SW, coupled with Fast Red Salt ITRN. One machine is to be used for impregnating and one for coupling. Then, the first lot of 300 lb requires 7 lb of Naphthol AS-SW, 8 pt of alcohol, 1.5 lb of dry caustic soda, and 4 pt of water. The machine is primed with 6 lb of dry caustic soda at 140 F. The yarn is naphtholated for 45 min. The material is then removed, salt rinsed, and coupled in a separate machine with 20 lb Fast Red Salt ITRN for 30 min.

The dyebath is saved for the succeeding lots, but additions must be made. Naphthol AS-SW possesses 45% substantivity; therefore, approximately 3 lb of the naphthol is taken up by the yarn. In addition, 50 gal of water is lost in the operation, containing another 12 oz, approximately, of naphthol. An addition is therefore made of 3 lb, 12 oz of Naphthol AS-SW, dissolved with 4 pt of alcohol, 1 lb of dry caustic soda, and 2 pt of water. It is also necessary to add 1 lb of caustic to the machine and to adjust the volume to the original starting level. Dyeing can then proceed, and the remaining lots are handled in the same manner as the first.

An important fact to remember is that all naphthols are of different substantivity. This fact must be taken into consideration before attempting to calculate the amounts needed for the original bath, or to calculate the additions to be made after each lot has been dyed.

Vat Dyes

General Characteristics

74. The vat dyes are the most important class of dyes for yarns or fabrics made from cellulosic fibers because materials dyed with these dyes have the best fastness properties. Vat dyes are particularly suited for wearing apparel as well as for other uses where the dye is exposed to washing, chlorine in laundering, light, and wear.

Generally, the vat dyes are water-insoluble pigments that are converted to the water-soluble form by reduction with alkaline hydrosulfite.

Preparation of Material

75. To obtain the full value, brilliancy, and fastness of the vat dyes on cotton, it is essential that the material be properly prepared before dyeing. While economic reasons may have some bearing upon the extent of the pretreatment, it is usually desirable to remove or modify the natural waxes and other impurities in cotton to a degree that will ensure satisfactory dye performance in the dyebath and give the desired fastness to the final product.

Dyeing

76. Vat dyes must be reduced to the soluble form with caustic soda and sodium hydrosulfite before they are applied. They are fixed on the fiber while in the reduced form, oxidized back to the insoluble form, and then soaped to obtain the final shade. Some of the many methods of applying vat dyes are discussed in detail later.

The true shades and maximum fastness of vat dyes are obtained by certain standard procedures. Oxidation, which causes the color to return to its insoluble form within the fiber, is accomplished in a number of ways. While exposure to air or rinsing will eventually oxidize the colors, speed and economy have made it standard practice to use chemical agents such as sodium or hydrogen peroxide or sodium perborate. Piece goods can, in addition to these methods, be oxidized with sodium bichromate and acetic acid, or they can be oxidized in continuous methods with carbon dioxide to neutralize the caustic, followed by a rinse. Temperature, time of treatment, and concentration of the agent selected depend on the dyeing method being used.

After oxidation and subsequent rinsing, the material should be soaped as close to the boil as possible with 0.125 oz per gallon of a surface-agent such as Duponol D Paste or Duponol RA, or 0.25 oz per gallon of soap. Soaping develops the shade completely and removes any superficially adhering surface color. During the soaping treatment a molecular rearrangement of the dye particles takes place within the fiber and brings about an increase in the fastness. The use of soap should be avoided on raw stock because of subsequent difficulty in carding and spinning. To assist the detergent action, it is usually desirable to add a small amount of an alkali, such as soda ash or tetrasodium pyrophosphate, to the soaping bath. A thorough rinsing to eliminate excess alkalinity is essential to maximum light fastness.

Special Treatments

77. The dyes listed under C. I. Vat Green 9, all of which are designed for black, require special treatment to produce the correct shade. After these dyes have been applied and oxidized as previously described, they appear as a deep green or green-black. In order to convert them to true blacks, they are treated either with a sodium hypochlorite solution containing 0.1% available chlorine, or, on the weight of the goods, with 2% to 3% sodium nitrite and 3% to 5% sulfuric acid 66 deg Baumé or 7.5% hydrochloric acid 18 to 20 deg Baumé, in place of the usual oxidation. Both treatments are made at room temperature. In either case, the material should be well rinsed to remove the chlorine or acid and then soaped at the boil.

78. Soft water is essential in circulating equipment for packages and beams, and it is advisable for all methods of vat dyeing. The reason for this is that all vat dyes are sensitive to some degree to aluminum, calcium, magnesium, and other metal salts. These salts can cause partial precipitation of the reduced form of most vat dyes, especially the anthraquinone blue types. When precipitation occurs, it results in poorer fastness to washing and crocking and in increased dyeing cost. There are many water-softening systems that are entirely satisfactory when properly controlled.

Where soft water is not available, the use of an appropriate surface-active agent in the scour or wet-out before dyeing, and in the dyebath and subsequent soaping, will materially aid in minimizing the difficulties caused by hard water. There are also a number of complex phosphates and organic sequestering agents that can be used to good advantage.

Control of Exhaust Rate

79. Dyeing formulas frequently specify a number of different dyes for a particular shade. To obtain best results when dyeing such combinations, it is advisable to use dyes having similar rates of exhaust. In batch operations it may sometimes be desirable to slow the rate of exhaust of some of the rapidly exhausting dyes. This can be accomplished by adding glue, lignin sulfonates, or other dispersing agents to the dyebath. Because all vat dyes are not retarded to the same extent by these agents, it is necessary to establish the kind and quantity of agent under actual mill conditions.

The rate of exhaust of most dyes can also be slowed by starting the dyeing at a low temperature, about 70 F to 80 F, and gradually raising it to the recommended dyeing temperature. Temperatures ranging from 180 F to 190 F can be used to obtain maximum penertation and leveling of the dye. Dyeing within this range is particularly applicable to packages, beams, hosiery, and knit goods; however, the effect of the high temperature on the stability of the dyes should be considered. In some cases, particularly with the Ponsol Blue types, a suitable dextrin or other protective agent should be used to protect the dye from over-reduction.

Dyeing Equipment

80. With the exception of small lots of material which are dyed in open tubs for specialty work, vat dyes are applied in special equipment that is designed for particular processes and forms of material. The current trend in the manufacture of machines is toward the use of stainless steel, which has little or no effect on the dyes and is relatively inert toward the reagents used in the dyebath. All vat-dyeing equipment is designed to effect economical production as well as to produce the best possible results consistent with the end use of the material.

Many different types of machinery have been designed for applying vat dyes. All of them attempt to provide the optimum conditions in dyeing. In using vat colors, it is necessary to chemically reduce the dyestuff at one stage in the dyeing process with sodium hydrosulfite and an alkali. In this stage, the oxygen of the air is combatting the reductive action of the hydrosulfite. While it is in the reduced state, the vat color has a high affinity for the cellulosic fiber; the higher the temperature of the dyebath, the greater this affinity, but the faster the hydrosulfite is destroyed.

Vat-dyeing equipment has been designed either to exclude air as much as possible, as in package-dyeing machines, or to apply the hydrosulfite only at the critical moment, just before high energy is given the material, as in the pad-steam process.

Package Dyeing

81. Cotton yarn in packages is dyed in a circulating machine equipped with a pump which forces the dye liquor through the material. The direction of flow can be controlled to permit the liquor to flow either from the inside to the outside of the package or in the reverse direction. The density of the package and the lay of the winding influence the uniformity of the dyeing obtained. All the packages in any load should be of approximately equal density to avoid excessive shading within the batch. On all circulating-type machines, special care should be taken to make certain that the pump is properly packed and is delivering its maximum flow. The volume of flow is more important than the pump pressure, and it should be as great as practical, since the levelness of the dyeing is directly related to the volume of flow.

The packages are boiled out in the machine for 15 to 20 min at 180 F to 190 F with the addition of an appropriate surface-active agent. Then the packages are rinsed and the temperature of the bath is adjusted to the dyeing temperature. This preparation prior to dyeing is recommended since it removes the soluble salts, tannins, and some of the waxes present in the cotton.

There are two general methods for dyeing packages with vat dyes: the pigment method and the reduced method.

Pigment Method

82. In the pigment method of package dyeing, the water dispersion of the dye is added to the machine and circulated for 10 to 20 min at the required dyeing temperature. There are many different dyeing assistants hat can be added to the dyebath, their selection depending on the depth of shade desired, the particular characteristics of the dye being used, and numerous other factors. Some of these assistants function as dispersing agents or retarding agents; others have the property of stabilizing the leuco of some of the vat dyes at high temperatures, as in the case of the indanthrene blues. Flake caustic soda, previously dissolved in water, is added in an amount of 0.5 oz to 1 oz per gallon of dyebath over a 10-min period. The caustic can be circulated for 5 to 10 min and then 0.5 oz to 1 oz per gallon of hydrosulfite is added over a 5- to 10-min period; or the two agents can be added alternately in several portions during 10 min. Reduction and fixation take place within ½ hr to 1 hr, depending on the temperature and the depth of shade. Heavy shades require more time, and it may be desirable in some cases to add 10% to 25% common salt to obtain a maximum exhaust of the dye.

After the dyeing cycle is complete, the bath is drained and the material is rinsed. If preferred, rinsing can be accomplished by overflowing the dyebath. A 15-min rinse is usually sufficient to remove any unfixed dye and most of the caustic soda. Oxidation is accomplished by adding 1% sodium perborate or hydrogen peroxide and heating to 120 F for about 10 min. After oxidation, the bath can be drained and the material soaped in a fresh bath, or a detergent can be added directly to the oxidation bath, in which case the temperature is raised to 180 F or 190 F and held for at least 10 min. Some dyers prefer to add 0.5% to 1% soda ash or 0.5% trisodium phosphate to the soaping bath. Soaping is followed by a thorough rinsing.

Reduced Method

83. With the reduced method, the packages are placed in the machine and the dyebath is primed or made up by the addition of caustic soda and hydrosulfite in the range of 0.5 oz to 1 oz per gallon of operating volume, depending on the dyes used and the depth of shade desired. The amount of caustic and hydrosulfite can also be calculated on the weight of the material. In a 10 to 1 volume, 4% to 7% each of caustic soda and hydrosulfite should be sufficient. The powder types of dyes are dispersed by pasting with a small amount of water; then they are

diluted with water at the desired temperature to a concentration of about 1 lb per gal. The paste types are similarly diluted with water to the same concentration. Dissolved caustic soda is added to provide a concentration of 2 to 4 oz per gal of reduction volume, followed by an equal amount of hydrosulfite added slowly with stirring. The types that dye best at temperatures of 120 F, or below, generally require less caustic soda.

As reduction takes place, the color of the dispersion will change and a solution ranging from a clear yellow, in the case of many of the thioindigoid types, to a deep blue, characteristic of some of the anthraquinone types, will result. Reduction is usually complete in 10 to 15 min, and then the reduced dye is added in two parts over a 10-min period to the primed dyebath. Circulation is continued for ½ hr to 1 hr for complete fixation of the dye. It may be desirable to add some salt with the heavy shades to obtain maximum exhaustion, particularly with those dyes that are applied at 120 F or lower.

After the dyeing cycle is complete, the bath is drained and the material rinsed. Oxidation and soaping are then accomplished in the same way as was described for the pigment method of dyeing. Soaping, of course, is followed by a thorough rinsing.

Beam Dyeing

84. Either the pigment method or the reduced method described for package dyeing can be used for beam dyeing. These two methods are similar. The beams should be uniformly wound and of such a density that the dyebath can circulate freely, but not so soft that channeling will occur. Throughout the process, care should be exercised in regulating the pressure in order to prevent channeling, which seriously impairs the uniform circulation of the dyebath. Steaming the beams in the dyeing machine, before the first water circulation, reduces their tendency to channel.

Raw-Stock Dyeing

85. Cotton raw stock is usually dyed in circulating machines in which the cotton remains stationary while the dye liquor is forced down through the load in one direction. The stock must be carefully loaded so that its resistance to flow is uniform, which will avoid channeling and uneven dyeing. Either the pigment method or the reduced method described under package dyeing can be used.

Oxidation with chrome and acetic acid is not recommended, because of its tendency to render the fiber harsh. Chip soap should not be used in the soaping operation. A surface-active agent can be added to the oxidizing bath and the temperature raised to 180 F or 190 F for 10 to 15 min, followed by a rinse.

A scour or wet-out with 0.1% Avitex AD, a textile-processing agent, is recommended, followed by a rinse before dyeing. This textile-processing agent has proved particularly valuable when dyeing raw stock in circulating machines, as it has a tendency to lessen the compressing action on the cotton by the one-directional flow, thereby retaining a loftier fiber for the subsequent carding and spinning operations. Circulating 0.1% to 0.2% of this product for 10 min in the final rinse after dyeing will greatly contribute to this desirable condition.

Warp Dyeing

86. Both long and short chain warps can be wet out at the boil by one passage through a bath containing 2 lb of soda ash and 4 oz of Avitex AD per 100 gal. The warp can then be dyed by the following method: The bath is sprung and one-fourth of the reduced dye is added. The warp is given one pass. Another portion of dye is added, and the warp is passed through the bath again, but this time the run is started with the opposite end of the warp. This process is repeated until all the dye is added. In some cases, particularly for long warps, an additional portion of the reduced dye is fed into the dyebath at regular intervals during the first pass, and during the running of subsequent passes. The material is then skied, rinsed, oxidized, and finished.

Newer methods for the continuous dyeing of warps require considerably less time to fix and build up the shade. The dry warp is passed through a suspension of the vat dye in water with enough wetting agent to produce instantaneous wetting, and then through a chemical bath containing caustic soda, hydrosulfite, and color. The warp next enters a steamer and is steamed for 20 to 30 sec. Sometimes it may be desirable to use a booster in the steamer to obtain optimum results. After leaving the steamer, the warp is rinsed, oxidized, and soaped.

Skein Dyeing

87. Skeins of soft-twisted yarns can be prepared for dyeing by giving them two turns at the boil in a bath containing 1 lb of soda ash and 4 oz of Avitex AD per 100 gal. Hard-twisted ply yarns, especially threads, are often given a kier boil. Skeins are customarily dyed in a skein-dyeing machine, but they can also be dyed in a hand tub. The skeins are entered into the spring bath, turned, and then lifted out while the reduced dye is added. The skeins are re-entered into the bath and dyeing continued until the color is exhausted. Because of the long bath some dyes may require the use of salt. Better penetration of hard-twisted yarns can be obtained by using the pigment method than is generally obtained by using the reduced method.

When dyeing in an open machine where the material is in contact with the air part of the time, increased amounts of hydrosulfite are necessary. An additional 0.25 to 0.5 oz of hydrosulfite per gallon of liquor is sufficient in most cases.

Preparation and Dyeing of Piece Goods

88. The careful preparation of cotton piece goods for dyeing is a major factor contributing to the fastness, penetration, and general appearance of the finished product. The extent of the preparation depends upon several factors, but the

usual steps in the preparation of cotton fabrics are the following: singeing; desizing; boil-off, which can be accomplished in jigs, open boil-off machines, continuous J-box boil-off, or kiers; mercerizing; and bleaching. It is particularly important that fabrics which are to be padded should be thoroughly absorbent.

Piece goods may be dyed by a variety of methods, each of which is classified as either discontinuous or continuous dyeing. Discontinuous dyeing includes the reduced-jig and pigment pad-jig methods. In continuous dyeing you'll find such methods as the reduced pad-booster continuous range, the pad-steam continuous process, the Williams unit method, and the vat-acid method.

Reduced-Jig Method

89. The reduced-jig method of dyeing piece goods is satisfactory for producing heavy shades where complete penetration is not of major importance. The material is wet out by two passes in the priming bath, which contains about two-thirds of the total requirement of caustic soda and hydrosulfite. For a 100-gal jig 6 to 8 lb of caustic soda and 8 to 12 lb of hydrosulfite should be adequate.

One-half of the reduced dye is added on the third pass and the remaining dye on the fourth pass. The material is given four or more passes through the dye liquor, rinsed for two passes with cold water, and oxidized. It is then rinsed free of oxidizing chemicals and thoroughly soaped.

Pad-Jig Method

90. Excellent penetration is one of the advantages of this method, and the shading of the material is also more uniform than that obtained by the reduced-jig method. The material is first padded with a water suspension of the vat dyes in pigment form at 100 F to 120 F. It may occasionally be desirable to add dispersing or other agents to the pigment-pad bath for specific purposes. A small amount of wetting agent is of assistance if the fabric is not particularly absorbent, or it may be desirable to add dispersing agents such as glue or sodium lignin sulfonates to minimize the effect of nonuniformly prepared material.

The padded material is usually batched into rolls of varying lengths, depending upon the thickness or weight of the fabric. The material is then transferred, without drying, to a jig and given four to six passes with 6 to 8 lb of caustic soda and 8 to 12 lb of hydrosulfite per 100 gal, at a temperature of 100 F to 160 F, the temperature depending upon the dyes being used. About 8 oz of a surface-active agent in the jig during reduction is recommended to produce a protective surface foam and to redisperse any oxidized dye. Oxidation and soaping are carried out in the same manner as prescribed for reduced-jig dyeing.

Reduced Pad-Booster Continuous Range

91. Another method is the reduced pad-booster continuous range. This method consists in padding the material with a solution of the reduced vat dye and then passing the material through re-reduction boxes where additional fixa-

tion and leveling take place. The re-reduction boxes contain caustic soda or soda ash, hydrosulfite, usually salt, and enough dye to establish an equilibrium for uniform shade and strength throughout the run. In dyeing bright blues, the use of salt may cause precipitation of the dye and should be avoided. The time that the fabric is immersed in the booster boxes depends upon the construction of the goods, the depth of shade being run, and the degree of fastness required. Marquisettes and voiles, for example, require a shorter time in the booster than heavy materials such as drills.

The fabric is then rinsed, oxidized, and soaped. In some cases the soaping is done in one run on the dyeing machine; in others, the material is rope soaped, the method varying with the equipment and the requirements of the individual plant. For the production of uniform dyeings with maximum fastness, it is essential that the temperature, alkalinity, hydrosulfite concentration, and amount of dye be accurately controlled in the booster bath.

Pad-Steam Continuous Dyeing Process

92. The pad-steam continuous dyeing process is widely used because of its many advantages over the older continuous dyeing methods. Some of these advantages are as follows: 1) Vat colors can be applied continuously in a full range of strengths to a wide variety of fabrics in either long or short yardages. 2) The appearance, color yield, and fastness properties of dyeings are equal to the best work obtained by other continuous methods. 3) The process maintains perfect uniformity of shade throughout the run. 4) Substantial savings in labor and chemicals are realized as compared with the pad-jig process. 5) Exhaustion problems and related difficulties are virtually eliminated, making the practical operation of the process very simple.

The unique feature of the pad-steam process is the extremely rapid reduction and fixation of vat dyes at a high temperature in an air-free steam chamber. The basic procedure is as follows: The prepared fabric is pigment padded with a water suspension of the vat dye; this operation is the same as for the pad-jig method previously discussed. The cloth can then be dried or left wet, depending upon its character and the shade being produced. If the material is to be dried, any type of equipment suitable for drying pigment-padded fabrics can be used, but the drying must be uniform as with other pigment-pad dyeing operations. The material then passes into a chemical pad containing a solution of caustic soda and hydrosulfite at a concentration of approximately 4 oz per gallon of each. The fabric is run directly from the chemical pad into the steam chamber, where, in a few seconds, the dye is reduced and fixed on the cloth. A sufficient flow of steam is necessary to prevent air from entering the unit. Uniform distribution of the steam over the fabric surface is important, and dripping of steam condensate on the fabric should be avoided. From the steam chamber, the dyed fabric passes through the conventional oxidation, soaping, rinsing, and drying operations.

Three variations of the pad-steam process are the following: 1) The fabric is pigment padded with dry chemicals, pad steamed, and finished. This method is particularly suitable for all types of flat fabrics. 2) The fabric is pigment padded with chemical solutions, pad steamed, and finished. This method is used for terry toweling, corduroy, and certain unmercerized flat fabrics. The drying step, which is difficult to carry out with pile fabrics, is eliminated. It is important that the padders be adjusted to give the chemical pad a higher pickup than the pigment pad so that the fabric can take up the necessary caustic and hydrosulfite from the chemical pad for development. When the difference in pickup is small, caustic soda is sometimes added to the pigment and hydrosulfite is fed with a dry feeder. Careful control should be exercised because some vat pigments can be coagulated by the caustic. 3) In another process, the dye is reduced with caustic and hydrosulfite and padded, after which the fabric is steamed. This process is called the reduced pad-steam and finish method. It is applicable to light and medium shades. The dye is reduced with caustic and hydrosulfite and padded, after which the fabric is steamed.

Williams Unit Method

93. The Williams unit method consists in padding the fabric with the dispersed vat pigment and in drying the fabric or entering it wet into the Williams unit, which contains sufficient dye to maintain equilibrium and caustic soda and hydrosulfite at a concentration of approximately 3 oz per gal. The reduction bath in the unit is maintained at 190 F to 195 F, and the cloth is immersed for about 15 sec, the length of time depending on the speed of the machine. After leaving the unit the fabric is rinsed, oxidized, and soaped.

Vat-Acid Method

94. The vat-acid method of applying vat dyes in pastel and light shades to piece goods is still sometimes used. Its advantages include freedom from specks and a smooth coverage that is either equal or superior to that obtained with vat pigment dispersions in pastel shades. The procedure consists in reducing the vat dye and then acidifying the reduced dye in the presence of a dispersing agent to produce a very fine dispersion of the acid leuco. The dispersion is padded and the cloth then processed wet or dry, depending on the circumstances. The cloth can be re-reduced on the jig with caustic and hydrosulfite, the same as for a conventional pigment, or else it can be padded with caustic and hydrosulfite followed by steaming or by developing on a Williams unit.

There are many variations in procedure for making the vat-acid dispersion. Of these the following is typical:

Reduce for 15 min at 120 F to 140 F in
  50 gal of water containing

x lb dye	3 lb hydrosulfite
3 lb caustic soda	5 lb dispersing agent

Strain the above reduced dye into
  50 gal of water at 75 F to 80 F containing
    5 lb dispersing agent
    6.5 lb glacial acetic acid
    1 lb textile processing agent
Good agitation during the mixing is necessary to obtain an optimum dispersion.

The vat dyes vary widely as to the concentration that can be made into a vat-acid dispersion. Best results are generally obtained at concentrations ranging below 2 to 3 oz per gal. Vat-acid dispersions have better stability at 80 F to 90 F than at higher temperatures.

Indigosols, Basic Dyes, and Oxidation Colors

Yarn Dyeing with Indigosols

95. Indigosols are the water-soluble sulfuric acid esters of the vat dyestuffs. They are applied to textiles from a water solution and are then converted to the original vat dyestuff by treatment with an oxidizing agent in acid solution. By this treatment they are made insoluble in water and therefore possess substantially the same fastness as the vat dyestuffs from which they are derived.

Indigosols may be applied to yarn skeins on the usual types of machines. The amount of dyestuff used depends on the depth required, usually from 0.25% to 1.0% of the weight of the material. The dyeing temperature is around 80 F; 50% to 100% common salt, and sometimes a small percentage of acetic acid, is added. Development is by the nitrite method, using 8 to 16 oz of sodium nitrite and 1 gal of sulfuric acid, 66 deg Baumé, per 100 gal of water, at 80 F for 20 min. The bath is then dropped and the yarn is rinsed, neutralized, and soaped

When indigosols are applied on the package machine, the dyeing is carried out in almost the same way as for direct colors. The temperature is maintained at 130 F, cooling to 80 F. Glauber's salt is used for exhaustion. The goods are then developed with 0.75% to 1%, by volume, of sulfuric acid, 66 deg Baumé, and with 0.1% to 0.2%, by volume, of sodium nitrite at 80 F for 10 min, followed by rinsing, neutralizing, and soaping.

Piece Dyeing

96. Piece goods are dyed with indigosols on the jig, then padded and continuously developed. When applied on the jig, the dissolved dyestuff is added in equal portions over two to four passes at 120 F. The required amounts of sodium nitrite and Glauber's salt are added after the dyeing has proceeded for 20 min. The temperature is allowed to drop over the remainder of the 45 min of dyeing time. The material then passes through a squeeze roll and into a bath containing 2 to 2.5 gal of sulfuric acid, 66 deg Baumé, per 100 gal, and 5 to 10 oz of sodium nitrite. The cloth is run in the bath at a temperature of 80 F to 140 F for one to

four passes, depending on how the dyestuff develops and on the depth of the shade desired. The material is finished by rinsing, neutralizing, and soaping.

When dyeing the goods continuously, a padder and a series of open boxes or Williams units are used. The material is run through the padder at high speeds. The padder contains a small volume of dye liquor, in order to minimize problems of exhaustion. The dye is padded with the addition of 0.5 oz to 1 oz of sodium nitrite per gallon, at 160 F. It is developed by running through 2%, by volume, of concentrated sulfuric acid at 120 F to 160 F. The time in contact with the acid may be only 2 to 3 sec, followed by 10 to 15 sec of skying before going into the open boxes for subsequent rinsing, neutralizing, and soaping.

Indigosols are important in the textile dyeing field because of the ease with which pale or pastel shades are obtained, with excellent fastness to washing, light, and chlorine. They are also important in wool dyeing, as the fastness properties of vat dyestuffs are obtained without the use of caustic soda, which is detrimental to wool.

Basic Dyestuffs

97. Basic dyestuffs contain unsubstituted or substituted amino or imino groups, which cause the dye to function as a positive ion in dilute acid solution. Most basic dyes are offered in the form of water-soluble chlorides, acetates, oxalates, sulfates, or zinc double salts. Some characteristic basic dyes are listed in Table 8. Although, as a group, the basic dyes constitute the least important class of dyes for cotton, they are used in dyeing leather and paper, and special basic dyes are widely used in dyeing Orlon and other acrylic fibers.

The fastness of basic dyes to light, washing, and rubbing leaves much to be desired. However, their tinctorial value and brightness are very high, and for this reason small percentages are often used for topping regular dyeings. With most cellulose products, this can be accomplished only by first applying a mordant to the material. The mordanting can be done with tannic acid and tartar emetic, but these are often replaced by Katanol O, a synthetic mordant resulting from the sulfuration of phenol.

TABLE 8

BASIC DYES

Dyestuff	C. I. Name
	BASIC
Auramine	Yellow 2
Safranine	Red 2
Rhodamine B	Violet 10
Crystal Violet	Violet 3
Methylene Blue	Blue 9
Nile Blue BXA	Blue 12
Brilliant Green	Green 1

Mordanting

98. The goods are immersed for 15 to 30 min in a bath containing 1% to 6% tannic acid on the weight of the fabric, at 140 F to 185 F. The amount of tannic acid depends on the depth of the dyeing to be done. The goods are allowed to remain overnight in a batched state or in the cooling bath. They are then extracted and treated in a cool bath containing tannic acid in an amount which is half that of the tartar emetic, for 30 min. After that the goods are rinsed well and dyed immediately or dried for future use.

When applying synthetic mordant, the material is entered into a bath containing 1.5% to 6% Katanol O solution at 160 F to 180 F. After the material has been circulated in the bath for 10 min, 5% to 40% common salt is added, and application of the mordant is continued in a cooling bath for 50 min. The goods are lifted and rinsed well in a cold solution containing 0.5% acetic acid (28% concentration), and 2% salt, on the weight of the fabric. The goods can then be dried or dyed directly.

Dyeing

99. Dyeing is started in a cold bath set with 1% to 4% acetic acid (28% concentration) and a nonionic dyeing assistant. The use of an anionic dyeing assistant would cause precipitation of the dyestuff. The dyestuff is added in small quantities from a well-dissolved solution at 5-min intervals. The temperature is gradually increased so that at the end of 1 hr it is 160 F, at which time the bath should be exhausted. Auramine, C. I. 655, requires a lower dyeing temperature and should not be raised above 120 F for dissolving or dyeing.

Oxidation Colors

100. Of the colors that are produced by oxidation, only aniline black is of importance. Aniline black is produced on the fiber by the oxidation of aniline or its homologues by means of chromates or chlorates, in the presence of metallic salts which serve as oxygen carriers. These dyestuffs have unequaled depth of shade and good fastness to light and washing, but they are subject to attack by sulfurous acid and perspiration. Aniline oil or aniline hydrochloride is oxidized in an acid medium with the help of an oxygen carrier such as sodium chlorate or sodium bichromate.

Dyeing may be done by padding the goods with a mixture of aniline oil, a suitable thickener, and an aqueous solution of aniline hydrochloride, potassium ferrocyanide, and sodium chlorate. The padded goods are dried and steamed for 2 to 3 min at 212 F. A subsequent treatment at 120 F with a solution of sodium dichromate and acetic acid completes the oxidation. The dyed goods are then rinsed and soaped in the usual manner.

Aniline black dyeing will cause some tendering of the fiber under the best conditions. This tendering can be minimized by careful balance of the ingredients of the padding liquor and by careful control over the drying and steaming temperatures. There should be no delay, after steaming and chroming, in washing and soaping the goods.

Mordant and Fiber-Reactive Dyes

Mordant Dyes

101. Mordant dyes are still used in textile printing, particularly on cotton cloth, and although their application in dyeing is very rare, they are of great historical interest. Dyeing with mordant colors was an important art in the past, especially the dyeing of cotton yarn with Alizarine Red, using aluminum salts as mordant. However, the naphthol dyes have almost completely supplanted this class of dyes.

Mordant colors have no affinity for cotton directly. The cotton is first impregnated with a salt, such as aluminum acetate or chromium acetate, and the cloth is dried and aged, whereby the salts are converted to the oxides. The dyes are then applied, and attach themselves to the aluminum oxide or chromium oxide.

The method of dyeing Alizarine Red involved several steps: oiling, mordanting, aging, dyeing, and chalking, followed by washing.

Dyeing on chromium mordant is less complicated. Cotton cloth may be dyed, as for white discharge printing, by combining a solution of the dyestuff with the mordant, usually chromium acetate, in a padding liquor. The goods are impregnated on the padder, dried, and then steamed or aged in steam.

The principle involved here is being exploited in the dyeing of polypropylene, using a most novel technique.

Mordant dyestuffs have considerable importance in the dyeing of wool.

Fiber-Reactive Dyes

102. Up to this time you have studied the dyeing of cotton with dyes which are considered to have affinity for the fiber:

1. Soluble dyes which are absorbed by the fiber and become attached to it by secondary attractions, or by aggregation in the fiber. This would explain the direct dyes.
2. Dyes which are rendered soluble in the dyebath by chemical reactions, and after absorption from the dye liquor, are insolubilized in the fiber. This would explain the vat dyes.
3. Dyes which are formed on the fiber by combination of soluble intermediates. Dyes so formed are insoluble. This refers to the naphthol dyes.
4. Dyes which have affinity only for a mordant, which is first applied to the fiber, as with mordant and basic dyes.

Now a new dyeing principle has been introduced, one which involves for the first time a true chemical reaction of the dyestuff with the cellulose, producing a stable union. Up to now, dyeing involved physical combinations of dye and fiber.

TABLE 9
FIBER-REACTIVE DYES

Dyestuff	C. I. Name
	REACTIVE
Cibacron Brilliant Yellow 3G-P	Yellow 2
Procion Yellow M-RS	Yellow 4
Procion Brilliant Yellow H-3GS	Yellow 6
Remazol Yellow RT	Yellow 16
Procion Brilliant Orange M-GS	Orange 1
Cibacron Brilliant Orange G-E	Orange 2
Cibacron Brilliant Red 3B-A	Red 4
Procion Scarlet H-RS	Red 13
Cibacron Scarlet 4G-P	Red 16
Cibacron Violet 2R-A	Violet 2
Procion Blue H-BS	Blue 2
Remazol Brilliant Blue R	Blue 19
Procion Orange Brown H-GS	Brown 1
Cibacron Black BG-A	Black 1

History and Nomenclature

103. The dyes which are known as fiber-reactive dyes were created in the 1930's, but were not at first exploited. They possess very low affinity for cotton in the usual dyebath containing salt, whether the bath is neutral or mildly alkaline. It is very probable that their reactive nature was not at first realized, since the reaction proceeds only in a strongly alkaline bath. It was not until about 1951 that dyes of this nature were found to be reactive, and methods of applying them were discovered.

The first reactive dyes to be marketed under this classification were the Procions of I.C.I. (Organics), Inc., and the Cibacrons of Ciba Chemical and Dye Company. Since then other groups of reactive dyes have been put on the market, such as the Reactones of Geigy Chemical Corporation, the Remazols of Carbic-Hoechst Corporation, the Drimarenes of Sandoz, Inc., the Cavalites of E. I. du Pont de Nemours & Company, Inc., the Levafix colors of Bayer Company, and the Genafix colors of General Aniline & Film Corporation.

Several different chemical-reactive groupings are illustrated in the dyes mentioned, but it can be said that the Procions and Cibacrons are similar to each other, likewise the Reactones and Drimarenes.

Some typical fiber-reactive dyes are listed in Table 9.

General Properties

104. The fiber-reactive dyes are generally bright, a result of their relatively simple structures. Because these dyes become chemically bound to the fiber, they show very good wash fastness.

Some of the fiber-reactive dyes have very good fastness to light; some do not. The earlier fiber-reactive dyes had poor fastness to chlorine, but some of the latest to be put on the market have good fastness. Although the dyes are not yet cheap in comparison to direct dyes, the methods of application are simple, resulting in savings in labor costs.

The fiber-reactive dyes are soluble in water, but unlike the direct dyes, have little or no affinity for cotton from a neutral or mildly alkaline dyebath containing salt. However, they do react with cellulose in a strongly alkaline bath, and it is this characteristic which dictates their methods of application.

Methods of Application

105. There are three general methods of applying reactive dyes: the exhaust, continuous, and pad-batch methods. One dominant factor in determining the method to be used is the form of the material to be dyed, whether yarn, raw stock, knit goods, or flat-woven piece goods. Another consideration is the dyeing equipment available in the mill.

The exhaust method is a batchwise process, and is used for yarn, raw stock, or knit goods. Yarn is generally dyed in package form and raw stock in a circulatory machine; knit goods are dyed in the beck. This method is also applicable to piece goods on the jig.

The material is first well scoured; then a fresh bath is made up and the dissolved dye is added. Common salt is then added in large amounts, up to 100% of the weight of the material. The salt acts as an exhausting agent. At the same time, alkali is added to the bath, in the form of soda ash or a mixture of soda ash and sodium bicarbonate. A long dye cycle is generally required to get the dye to exhaust.

The amount of salt and alkali used is determined by the type of fiber-reactive dye. There are two general types, the cold-dyeing and hot-dyeing types. Dyestuff manufacturers designate the two types by letters. For example, I.C.I. designates its cold-dyeing types as Procion M dyes, and its hot-dyeing types as Procion H dyes.

Typical applications would be as follows. To dye 2% Procion Brilliant Red M-5B on cotton yarn, dissolve 60 parts of salt per 1000 parts of water, while adjusting the temperature to 105 F. Run the liquor through the goods for 10 min. Add predissolved dye and run 30 min. Add 5 parts of soda ash per 1000 parts of water in two portions. Run 40 min and wash off.

To dye 2% Procion Brilliant Red H-3B, dissolve 80 parts of salt per 1000 parts of liquor in the dyeing machine, while bringing the temperature to 105 F. Add predissolved dye and run 10 min. Add 20 parts of soda ash (or 1 part of caustic soda flakes) per 1000 parts of water and raise the temperature to 175 F for 40 min; then wash off.

106. The continuous dyeing method affords the piece-goods dyer a simple way

to produce bright shades on good yardage. There are two alternatives in continuous dyeing. One is to pad the dye solution onto the cloth, and then dry. Pad a second time with a strongly alkaline solution, using 1⅓ oz of caustic soda and 40 oz of common salt per gallon, and pass the wet cloth through a steam chamber; then wash the cloth.

In the second alternative, the alkali is introduced directly into the dye solution. For the cold-dyeing types of dyestuff, pad the cloth with 10 parts of dyestuff (predissolved) and 10 parts of sodium bicarbonate per 1000 parts of water, dry at 260 F for 2 min, and then wash. For the hot-dyeing types, pad the cloth with 10 parts of dyestuff (predissolved), 200 parts of urea, 20 parts of soda ash per 1000 parts of water; dry the cloth, cure in a hot oven for 3 min at 280 F, and wash.

107. The pad-batch method is applicable to piece goods. The dyestuff is dissolved and added to the padding liquor. Soda ash is also added to the liquor. After padding, the cloth is batched up wet on large rolls. The rolls are kept warm for several hours, usually by introducing into a hot, moist chamber, where they are turned slowly to prevent draining of the pad liquor to one side. Finally, the rolls are unwound and the cloth is washed.

In none of these methods is there found to be 100% dye fixation. Some of the dye is always lost in the final washing.

Uses

108. The fiber-reactive dyes are finding new uses, especially where fiber blends and mixed-fiber fabrics are processed. For example, in dyeing cotton-nylon blends, it has been found possible to dye the cotton and reserve the nylon. Blends of this type are encountered in filling-stretch nylon-cotton denims, where continuous processing is feasible, and also in warp-stretch nylon-cotton blends, which are best handled by the exhaust-dyeing method in the beck.

In dyeing polyester-cotton fabrics, it has been advantageous to dye the polyester by the thermosol method and the cotton with fiber-reactive dyes in a two-step process.

Cotton is dyed as yarn, thread, raw stock, hosiery, knit goods, and piece goods. Rayon is also readily dyed, as are Avril and Zantrel, which are modified rayons.

Textile Dyeing

Serial 5508A PART 1 Edition 1

Examination Questions

Notice to Students.—Study this instruction text thoroughly before you answer the following questions. Read each question carefully and be sure you understand it; then write the best answer you can. Some of the questions are provided with a multiple choice of answers. Pick out the correct answer, and write down the letter (A), (B), (C), or (D), as the case may be, together with the number of the question. If the answer involves a mathematical solution, show enough of your work to indicate how you obtained your answer. When you complete your work, examine it closely, correct all the errors you can find, and see that every question is answered; then mail your work to us. DO NOT HOLD IT until another examination is ready.

1. Naphthol dye powder should be safely stored by
   - *A.* covering with a damp cloth.
   - *B.* keeping in glass bottles in a well-lighted room.
   - *C.* putting in airtight barrels in a cool place.
   - *D.* placing in a special oven, where it is kept warm. (5%)

2. When direct dyes are to be dissolved, it is advisable to
   - *A.* use a reducing agent.
   - *B.* let the mixture stand for at least 48 hr.
   - *C.* use live steam to heat and stir the mixture until the dye is completely in solution.
   - *D.* paste the dyestuff with hydrosulfite. (5%)

3. In order to put fast-color salts into solution
   - *A.* live steam is used to heat and stir the mixture.
   - *B.* the salts are first pasted with lukewarm water and then diluted immediately with cold water.
   - *C.* the salts must first be pasted with alcohol.
   - *D.* the salts must be strained prior to being dissolved. (5%)

4. Packages of dyes for household use often contain
   - *A.* direct dyes, which are easy to apply.
   - *B.* vat dyes, because of their fastness properties.
   - *C.* natural dyes, which have always been used for this purpose.
   - *D.* basic dyes, which produce brilliant shades. (5%)

5. Naphthol AS-BR has maximum exhaust at
   - *A.* 100 F. *C.* 95 F.
   - *B.* 80 F. *D.* 120 F. (5%)

6. A batch of goods has been dyed with Benzo Blue RW, C. I. 512. To improve the light fastness of the goods,
   - *A.* an additional 20% of common salt should be added to the dyebath.
   - *B.* a fresh bath containing copper sulfate and acetic acid should be used for aftertreatment.
   - *C.* the goods should be treated with formaldehyde and formic acid.
   - *D.* an aftertreatment with sodium bichromate is needed. (5%)

7. Ten pieces of cotton dress goods have been naphtholated by padding and drying. They are then salt rinsed prior to coupling. The purpose of the salt rinse is
   - *A.* to remove the acidity from the fabric.
   - *B.* to remove the excess alkalinity, as well as the naphthol, from the fabric.
   - *C.* to remove the naphthol but retain the alkalinity on the fabric.
   - *D.* to remove the excess alkalinity but retain the naphthol on the fabric. (5%)

8. List the chemicals to be used, and the amounts needed, to dye 5000 lb of cotton material with a bright-yellow direct dye. (18%)

9. Two pieces of cotton gray goods are to be processed. Piece A is an 8-oz twill to be used for work clothes and to be dyed sulfur black on the jigs. Piece B is a 4-oz broadcloth to be made into men's dress shirts. Explain how preparations before dyeing would differ for *A* and *B*. (8%)

10. What method would you use to apply vat dyes to cotton piece goods if you wanted excellent penetration and uniform shading? (5%)

11. Some piece goods have been dyed with sulfur dyes. There is not time to dry the goods before the mill closes down for the weekend, and the goods will remain in a warm, moist room. What can be done to prevent the dyestuff from oxidizing? (8%)

12. What difference in principle is there between the Ferris wheel yarn-dyeing machine and the package yarn-dyeing machine? (6%)

13. List the materials and the amounts needed to prepare 500 gal of an aftertreating solution to improve the light fastness of a blue material dyed with naphthol dyestuff. (10%)

14. You are dyeing goods with sulfur dyes. During the dyeing cycle, portions of the goods are exposed to the air. What is likely to be the result of this exposure? (5%)

15. A dye jig is shown in Fig. 3 of this text. Where is the dyeing actually done in this type of machine? (5%)

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