International Correspondence Schools, Scranton, Pa.

Textile Dyeing

By

HERMAN P. BAUMANN, Ch.E.
American Aniline Products, Inc.

and

WILLIAM WYGAND
E. I. du Pont de Nemours & Company

"The higher men climb, the longer their working day. And to keep at the top is harder, almost, than to get there. There are no 'office hours' for leaders."
                                    —Cardinal Gibbons

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But for the man who has found the job he loves, work is no longer "labor." And learning more about that job becomes a thrilling, exciting adventure.

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PART 2

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What This Text Covers . . .

This·brief outline of the contents of this text will help you to plan your studies. By checking off each section as you complete it, you will know exactly where to start when you pick up your text again.

5508B

Textile Dyeing

PART 2

Wool Dyeing

Structure of Wool

1. Wool dyeing differs in several respects from cotton dyeing. In order to understand the problems, it will be helpful to review those physical and chemical properties of wool that influence the dyeing process.

Microscopic study of wool fibers shows the wool to consist of three parts: 1) external scales, or cuticle, 2) cortex, or body substance, and 3) medulla, or central pith. All these parts are visible when cross sections of the wool fiber are prepared for the microscope.

Merino wool fibers are shown in Fig. 1 as they appear under a microscope when magnified 800 times. Each wool fiber appears as a rodlike shape and is covered with scales projecting toward the tip of the fiber. The scales play a major role in the felting of wool.
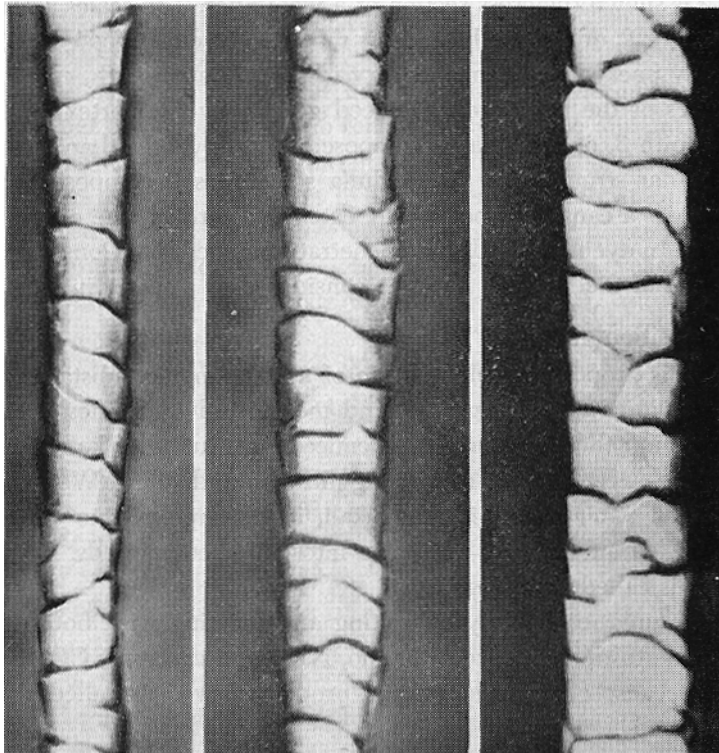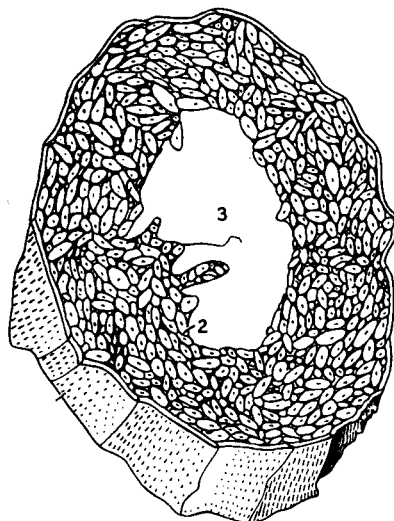

FIG. 1. WOOL FIBERS

1. scales   2. cortex   3. medulla

FIG. 2. CROSS SECTION OF A WOOL FIBER

2. In Fig. 2 is shown the cross section of a wool fiber. The scales 1 are on the outside. The cortex 2, or body substance, is made up of elongated 'cells, or pores. These are tightly packed together and vary in size. The strength, elasticity, and dyeing properties of the wool are influenced greatly by the cortex of the fiber.

The central pith 3, or medulla, is composed of cells larger than those of the cortex. The cellular structure of the medulla sometimes decomposes and in its place there appears a canal, or open space, extending through the central portion of the wool fiber. In dyeing, liquids may penetrate the medulla. Consequently, the size and structure of the medulla must be considered as a factor in wool dyeing.

Chemical Composition of Wool

3. Wool that is properly cleaned is free of accompanying substances such as suint (wool perspiration), wool grease, and mechanical impurities. Clean wool consists of a protein called keratin. The chemical constitution of keratin is chiefly a mixture of complex compounds containing nitrogen and sulfur. When keratin is in the presence of water containing an alkali, it decomposes into a number of organic acids, called amino acids, and also into sulfur compounds. This decomposition process is called hydrolysis.

Wool has the unique property of uniting and reacting with both acids and alkalis. This is due to the presence of amino, NH_2, and carboxyl, COOH, groups in the keratin. Because of its structure and properties, wool is called an amphoteric colloid by the chemist.

Action of Acids on Wool

4. Wool has a strong chemical affinity for acids, both mineral and organic.

The absorption of acids by wool is related to the molecular weights of the acids and to their degree of dissociation, or hydrogen ion concentration (pH). For example, sulfuric acid, a strong acid, has a greater degree of affinity for wool than does acetic acid, which is a weak acid having a low degree of ionization.

Dilute mineral acids, sulfuric and hydrochloric, are much alike in their action on wool, and they are readily absorbed. They differ in that hydrochloric acid can be removed more easily by washing than sulfuric acid, which is never completely removed from wool. Dilute solutions of sulfuric acid may be boiled with wool over a period of several hours without any serious effects. However, increased concentrations of sulfuric acid produce a corresponding loss in tensile strength. Complete chemical degradation results at elevated or boiling temperature if the boiling is continued for a period of time.

Dilute nitric acid shows a different behavior on wool when heated, imparting a yellow color due to the formation of nitrous acid; it also imparts a harsh hand. Hot concentrated nitric acid will completely destroy wool.

Organic acids such as acetic, formic, oxalic, and hydroxyacetic are considerably milder in their actions on wool. Also, because of their lesser acidity, they find use in the application of certain types of wool dyes.

Action of Alkalis on Wool

5. Alkaline solutions in general have a noticeably harmful effect on wool, resulting in fiber damage and loss in tensile strength. The amount of harm varies with the concentration, temperature, and duration of the action.

Sodium hydroxide or potassium hydroxide is extremely injurious to wool. A 5% solution at the boil will completely dissolve wool. Carbonates such as sodium carbonate are much milder in their action on wool. For this reason they are used in wool scouring at low temperatures not above 120 F, and for neutralizing carbonized or acid wools.

Of all the common alkalis, ammonium hydroxide has the mildest action on wool, and as a result it finds considerable use in wool dyeing. Nevertheless, when using alkalis on wool it is necessary to exercise care, in order to retard fiber degradation. In wool boiled for 1 hr at pH 8.5 to 9.0, a fiber damage of 25% has been noted. In piece dyeing, permanent folds result from boiling in an alkaline pH. Such folds, when severe, cannot be removed by wetting out and refinishing.

Swelling of Wool

6. An important characteristic of the wool fiber is its ability to swell when immersed in water and in solutions of acids and alkalis. Swelling permits the tightly packed micelles of the cortex to expand, or enlarge, owing to the osmotic pressure built up within the fiber. As the temperature of the water is raised above 120 F there is a corresponding increase in swelling. The swelling reaches its maximum extent at 212 F.

Wool increases its swelling correspondingly with an increase in hydrogen ion concentration. With acid solutions, swelling is greatest at pH 1.5. The fiber diameter at this point will be about 50% greater than its original diameter. At pH 10, with sodium hydroxide, swelling increases to about 60%. The swelling of wool is of considerable importance in dyeing, because the wool scales are thought to act as filters for dye molecules deposited on the surface of the wool fibers. Swelling of the wool permits greater mobility and diffusion of the dye molecules within the micelles, thus playing an important part in uniform dyeing. The temperature of 212 F is standard for wool dyeing, because swelling is at the maximum at this temperature.

Preparation for Dyeing

7. Complete and uniform removal of natural and foreign impurities, and the removal of lubricating and sizing materials added to facilitate the processing of the wool — these are essential to successful dyeing. Very often, poor dyeing results can be attributed to insufficient removal of oils and soaps from raw stock and piece goods. In this respect the requirements for piece goods are much more exacting than those for raw stock. The oil and soap contents of piece goods should be kept at a minimum.

Acid Dyeing

Classification of Dyes

8. The dyes used in the dyeing of wool may be grouped into six different classes. These classes of dyes are 1) acid dyes, which may be subdivided into level dyeing, intermediate level dyeing, and milling, or neutral, dyeing dyes; 2) chrome, or mordant acid, dyes; 3) metalized dyes; 4) natural dyes; 5) indigo dyes; and 6) indigosols.

Theory of Dyeing

9. Even before the introduction of synthetic dyes, researchers had attempted to formulate theories to explain wool dyeing. No less than five theories were offered. These were the 1) mechanical, 2) chemical, 3) solid solution, 4) colloidal absorption, and 5) electrical theories. The mechanical theory defined dyeing as a condition in which the dye was mechanically held or absorbed by the pores of the wool fibers. The chemical theory considered dyeing to be the result of a definite chemical reaction between the wool and the dye. The solid solution theory explained that the wool fiber was simply extracting the dye from the solution. According to the colloidal and electrical theories the dye and the wool are considered as colloids of different electrical charge, with the result that they are attracted to each other. If the last two theories are true, precipitation of the dye should be hastened in the presence of electrolytes.

As a result of intensive research in wool dyeing, it has been proved that dyeing

is not accomplished according to any single one of the five theories, but that the process of dyeing reflects a combination of the theories. There is now wide agreement that the wool-dyeing process is one of chemical reaction determined by the chemical constitution and structure of the dyestuff, but that electrolytes, pH, and the physical properties of the wool have a part in the process.

Chemistry of Acid Dyes

10. The majority of acid dyes are members of the azo class containing the axo chromophore group ($N = N$). Other classes of importance are the anthraquinone and the triphenylmethane. Dyes of lesser importance are the nitro, azine, and xanthene. Substances which contain chromophores are capable of producing color, but they are not capable of acting as a dye in themselves. As such they are called chromogens or compounds which can be converted into dyes.

By the addition of a salt-forming group, or auxochrome, to the chromogen, a definite color of dye is produced. Such salt-forming groups are the sulfonic, SO_3H; carboxyl, $COOH$; nitro, NO_2; amine, NH_2; and hydroxyl, OH. A characteristic dye produced in this way is C.I. Acid Yellow 36.

11. Acid dyes are generally the sodium salts of color acids, the majority of which contain sulfonic acid. The sulfonic acid group is responsible for the solubility of acid dyes. As many as one to four groups may be present in a dye molecule.

Characteristic of the azo class are such colors as yellow, orange, scarlet, and red. Blue dyes are of lesser importance in this group. The anthraquinone group contains fast-to-light blues which are frequently used in acid dyeing. In the triphenylmethane group are brilliant shades of blue, green, and violet.

Theory of Level Dyeing

12. More than half of the acid dyes are molecularly dispersed dyes of molecular weights ranging from 300 to 800. They do not exhibit any degree of dye aggregation. Level-dyeing acid dyes, being of extremely minute particle size, have comparatively easy access into the pores of the wool fiber. Because wool has a pronounced affinity for strong electrolytes such as sulfuric acid, it also has an affinity for acid dyes, these being the sodium salts of strong acids, all of which possess electrolytic properties.

The affinity of wool for acid dyes varies with the dyes. Sulfuric acid is known to combine chemically with the basic side chains of the wool, breaking down the salt linkages. This reaction makes it possible for the sulfonic group of the acid dyes to combine with the amino, or basic, groups of the wool. Since the sulfuric acid exerts a high degree of dissociation, it reacts with the wool first. As the dyeing progresses, the acid leaves its position and allows the dye ion to combine with the amino groups. In this way exhaustion of the dye bath is brought about.

13. To illustrate the chemical affinity of acid dyes for wool, a 5-gram sample of worsted cloth was immersed in a dye bath of 1% Orange G, C.I. Acid Orange 10, and allowed to stand at room temperature for 72 hr. The water-to-wool ratio was 20 to 1. The amount of dye used was calculated on the weight of the material. Spectrophotometric measurements made of the dye solution after the designated dyeing period showed that 42% of the dye had been removed from the dye bath as a result of direct chemical combination with the wool.

Another dye bath, similar to the one just described, was prepared. In addition to the other ingredients, 4% sulfuric acid was put into the bath and the material boiled for 1 hr. Spectrophotometric measurements made of the exhausted dye bath revealed that 89% of the dye had been removed from the bath. The dye had chemically combined with the wool.

14. Although exhaustion of the dye bath is obtained with sulfuric acid, distribution of the dye ion is not uniform within the pores of the wool fiber. The resulting dyeing will have a skittery, or unsolid and streaky, appearance. However, with the addition of 5% to 10% Glauber's salt, uniform distribution of the dye ions is obtained. Glauber's salt acts as a retarding or leveling agent, and being a neutral salt, it retards swelling of the wool. Its function as a leveling agent is promoted by its SO_4 ion, which enters into competition with the dye ion for available space with the basic groups of the wool.

The following level-dyeing experiment will serve to illustrate the characteristic action of Glauber's salt. A 5-gram sample of worsted cloth was dyed at the boil for 1 hr with 1% Tartrazine, C.I. Acid Yellow 23. The water-to-wool ratio was 20 to 1. The dyed sample was washed and placed in a vessel together with a similar, but undyed, sample. Water was added until the vessel contained a 20-to-1 proportion of water to wool. Then 10% Glauber's salt and 2% sulfuric acid were added, and the samples boiled for 1½ hr. The experiment was repeated with the Glauber's salt omitted. Spectrophotometric reflectance measurements were then made. The results showed that 70% of the dye from the dyed sample had migrated to the undyed sample with Glauber's salt present. Without the presence of Glauber's salt, only 25% of the dye transferred from the dyed to the undyed sample. Similar experiments in leveling made with 0.25% Xylene Light Yellow 2G, C.I. Acid Yellow 17, showed 95% dye transference from the initially dyed to the undyed sample with Glauber's salt, and only 55% dye redistribution without Glauber's salt.

15. Acetic acid, a weak electrolyte having a low degree of dissociation, is unsatisfactory for use as an exhaustion agent for level-dyeing acid dyes. Dyeings made at the boil for 1 hr with 1% Xylene Light Yellow 2G, C.I. Acid Yellow 17, 10% Glauber's salt, and 2% sulfuric acid showed that 90% of the dye had been removed from the dye bath. In a similar dyeing, in which 4% acetic acid (56%

strength) was substituted for the sulfuric acid, only 58% of the dye was exhausted from the dye bath. Complete exhaustion of the acid dyes, particularly for medium and dark shades, does not occur in plant work. In plant work an increase in the amounts of mineral acid results in lower exhaustion rates

Properties of Acid Dyes

16. Level-dyeing acid dyes are characterized by their production of wide ranges of brilliant colors. The fastness to light of acid dyes varies, ranging from poor to excellent. Generally, light shades are apt to show a fastness inferior to that of darker shades, which are satisfactory for most uses. Most bright shades of green, blue, and violet are of poor fastness to light.

Acid dyes exhibit poor fastness to washing, alkalis, scouring, and fulling. As a class, acid dyes are easily injured by alkaline perspiration, particularly medium-to-dark shades. On the other hand, their fastness to acids, hot pressing, dry cleaning, carbonizing, and rubbing, or crocking, is satisfactory. With wet crocking, however, darker shades show some bleeding.

Uses for Acid Dyes

17. Acid dyes are used mostly for children's and women's wear fabrics whose prime requisites are fastness to dry cleaning and moderate fastness to light. They are also used for knitting yarns, and for coloring felts for women's and men's hats. Often acid dyes are used for dyeing materials other than those just mentioned. When used on fabrics that are liable to absorb perspiration and must therefore be washed, acid dyes cause consumer dissatisfaction, since their fastness to light and washing are not good.

Three Groups of Acid Dyes

18. For convenience in discussing the acid dyes, they are here divided into groups A, B, and C. Group A represents the best level-dyeing acid dyes. Group B represents the intermediate level-dyeing, or acetic acid, colors. Group C contains the poorest level-dyeing, or neutral, dyes — that is, those dyes which do not possess the property of migrating in Glauber's salt, as do those of Groups A and B.

Some commonly used acid dyes of Group A are listed in Table 1. The Colour Index (C.I.) generic names of each are also given. All dyestuffs with the same C.I. name have the same chemical constitution.

Practical Level Dyeing

19. Acid dyes are applied to wool from an acid bath. Sulfuric acid of 66 deg (degrees) Baumé is used almost exclusively. The usual amounts employed are 2% to 4%, depending on the depth of the shade, together with 10% Glauber's salt. The chemicals and dyes used to obtain a desired shade are calculated on the amount of material being dyed.

After the material has been thoroughly wet out with the dyeing assistants, the

TABLE 1

ACID DYES

Dyestuff	C. I. Name
	ACID
Naphthol Yellow S	Yellow 1
Chinoline Yellow D Conc.	Yellow 3
Xylene Light Yellow 2G	Yellow 17
Tartrazine	Yellow 23
Acid Orange II	Orange 7
Acid Orange RO	Orange 8
Wool Orange G	Orange 10
Amacid Phloxine G Ex.	Red 1
Azo Eosine G	Red 4
Ponceau 4R	Red 18
Amaranth	Red 27
Croceine Scarlet MOO	Red 73
Victoria Fast Violet RRN Conc.	Violet 1
Chromotrope 5B	Violet 6
Violamine RD	Violet 9
Formyl Violet S4BA	Violet 17
Wool Violet 4BN	Violet 49
Kiton Pure Blue V	Blue 1
Alphazurine FG	Blue 9
Alizarine Astrol B	Blue 27
Alizarine Sapphire SE	Blue 43
Alizarine Sapphire BN	Blue 45
Naphthol Green B	Green 1
Brilliant Milling Green B	Green 9
Wool Green S	Green 50
Amacid Black 10BR Conc.	Black 1

dyestuff, previously dissolved in boiling-water, is added and the dye bath raised to the boil in 30 to 45 min. Boiling is continued for 1 hr or longer. The length of the boil varies with the type of material being dyed and the dyeing equipment used. With stock or package dyeing, a boiling period of 1 hr to $1\frac{1}{4}$ hr is usually satisfactory. In dyeing piece goods, longer boiling periods are necessary, the time being determined by the construction and weight of the fabric.

Sodium bisulfate may be used as a substitute for sulfuric acid. It lends itself to safer handling, being a solid, and it is readily soluble in water. Sodium bisulfate is used to replace an equivalent amount of sulfuric acid and Glauber's salt. The pH of an acid dye bath falls between 2.5 and 3.0.

20. Piece goods containing decoration yarns of cotton and rayon are dyed with 2% to 5% formic acid of 90% strength. The use of sulfuric acid should be avoided, because mineral acids cause a tendering of the cellulose fibers. Organic acids do not impair fiber strength, and they are safe to use.

Carbonized material may be dyed by utilizing the sulfuric acid contained in

TABLE 2

ACETIC ACID DYES

Dyestuff	C. I. Name
	ACID
Fast Silk Yellow G	Orange 1
Supramine Red GGA	Orange 19
Polar Orange GS Conc.	Orange 49
Polar Yellow R Conc.	Orange 63
Amacid Azo Yellow G Ex.	Yellow 63
Amacid Red 3B Conc.	Red 66
Xylene Milling Red R	Red 89
Amacid Milling Brown R Supra	Brown 2
Amacid Resorcine Brown 2R Conc.	Brown 14
Alizarine Supra Blue A	Blue 25
Alizarine Brilliant Blue R Conc.	Blue 67
Milling Fast Black 2B	Black 24
Wool Blue Black 6B Conc.	Black 26
Alizarine Light Grey 2BLW	Black 48

them. However, carbonized materials contain approximately 6% acid, which is generally more than is necessary for acid dyeing. The excess acid can be removed by treating the wool with water at 120 F to 180 F for 30 min and then washing it. This treatment removes about one-half of the acid present. To the dye bath is then added 10% Glauber's salt, and the necessary percentage of dye, previously dissolved in boiling water. The temperature is then raised to the boil, and boiling continued for the necessary length of time.

Some carbonizing is being done with aluminum chloride, but this method is applied to such a small volume of material that it is not of general interest.

Intermediate Level Dyeing

21. About one-third of the acid dyes, classified as Group B, exhibit only intermediate level-dyeing properties. These properties are considered to be related to the molecular structure of the dye, which is composed of larger molecules and is subject to aggregation, unlike the Group A level-dyeing acid dyes.

Sulfuric acid, if used as an exhausting agent, would cause a rapid deposition of the dye, and result in a streaky and unsolid appearance. Redistrbution of the dye ion within the cellular structure of the wool fiber is considerably lessened because of its molecular size and the extent of aggregation. The use of a weaker acid, such as acetic acid, aids materially in a gradual deposition of the dye. Owing to the use of acetic acid, the dyes in this group are often called acetic acid dyes.

Acetic Acid Dyes

22. Intermediate level-dyeing acid dyes exhibit properties similar to those of the level-dyeing acid dyes. But owing to their molecular structure, which is of a somewhat greater complexity, they display slightly improved properties to such

wet treatments as washing and scouring, and to treatments which require the application of alkalis.

Some typical acetic acid, or intermediate level-dyeing, dyes are listed in Table 2.

Practical Intermediate Dyeing

23. The application of acetic acid dyes is similar to that of the level-dyeing acid dyes, with the exception of the exhausting agent used. The bath is prepared with 5% to 10% Glauber's salt, 2% to 4% acetic acid of 56% strength, and the necessary percentage of dye. The bath is raised to the boil in 45 to 60 min and boiling continued for the necessary period.

Dyes that are difficult to exhaust with acetic acid may require the use of 1% to 2% formic acid. Phosphoric acid may be used in place of the formic acid in the same amounts. Phosphoric acid has the further advantage that it prevents the formation of iron stains and the dulling of delicate bright shades. The pH of an acetic acid dye bath is between 3.5 and 4.0.

Neutral Dyeing

24. Neutral, or milling, dyes are classified as Group C. They constitute only a small number of the acid dyes. Although they are still the sodium salts of the color acids, their molecular structure is of an increasing chemical complexity that contributes to colloidal aggregation. With aggregating dyes this characteristic is very strong at low temperatures, but at temperatures near or at the boil molecular aggregation is considerably lessened.

In the presence of electrolytes, such as sulfuric acid or Glauber's salt, there is further molecular aggregation; this results in streaky and unsolid dyeings. Owing to their large molecular size, neutral dyes do not level off as do the level-dyeing acid dyes; consequently, once they have gained entrance into the pores of the wool fibers, they become permanently entrenched. In order to promote uniform application of neutral dyes, it is necessary to retard the chemical affinity of the acid dyes for the wool fiber until such time as the wool is in the best possible condition to assist in the uniform diffusion of the dye ion.

Favorable dyeing conditions are obtained by applying the neutral colors from a slightly alkaline or neutral bath; at this pH their affinity for wool is decreased. The temperature is then gradually raised to the boil, at which point maximum swelling of the wool fiber is attained. On continued boiling, the dye bath becomes progressively acid, thus promoting exhaustion. Unlike level-dyeing acid dyes, where leveling is obtained by continued boiling, neutral dyes are uniformly distributed by extending the time before the boil, with a gradual change in pH from 7.5 or 7.0, which is slightly alkaline, to 6.5 or 5.5, which is slightly acid. Glauber's salt is not satisfactory as a dyeing assistant for neutral dyes. There are, however, a number of ammonium salts, such as ammonium sulfate, ammonium
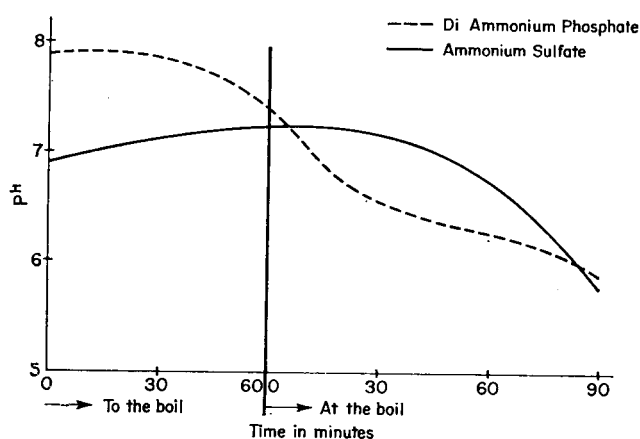
FIG. 3. DYEING ASSISTANTS

acetate, and monoammonium and diammonium phosphates, which comply with the requirements in the application of neutral dyes.

25. Ammonium sulfate is employed as a dyeing assistant for neutral dyes. This chemical loses its ammonia upon boiling, and sulfuric acid results. However, as wool has a pronounced affinity for acids, the sulfuric acid will be absorbed by the wool, resulting in premature acidity and promoting unwanted exhaustion at the start of the dyeing. Such a condition is corrected by adding 0.5% to 2% ammonia, producing a slightly alkaline pH at the start of the dyeing, which, on continued boiling, becomes slightly acid.

Ammonium acetate, the salt of a strong base and a weak acid, serves as an ideal assistant for neutral dyes. Since the acetic acid liberated has very little affinity for wool, controlled pH during the dyeing period is accomplished. The acetic acid maintains the balance at the start of the dyeing. Upon continued boiling, the acetic acid causes exhaustion of the dye bath.

The use of monoammonium phosphate for neutral dyeing has also been proposed. With highly colloidal acid dyes, however, the pH range of monoammonium phosphate, 5.5 to 6.0, is not satisfactory for uniform deposition of the dye ion. The addition of 2% ammonia will keep the pH range of monoammonium phosphate within the limits necessary to produce satisfactory results.

Diammonium phosphate, a neutral salt possessing excellent buffering properties, serves as an ideal assistant for the application of colloidal dyes to wool. Its decomposition on boiling is gradual, with a corresponding loss of ammonia. The pH limits of diammonium phosphate extend from about 6.0 on continued boiling to about 7.8 at room temperature. The action can be clearly seen in Fig. 3, which illustrates the pH, function of diammonium phosphate as compared with that of ammonium sulfate.

TABLE 3

NEUTRAL DYES

Dyestuff	C. I. Name
	ACID
Milling Yellow O	Yellow 38
Milling Yellow 5G	Yellow 40
Polar Red G Conc.	Red 85
Acid Anthracene Red G	Red 97
Polar Red R Conc.	Red 99
Milling Red PBX	Red 167
Cloth Fast Blue R Ex. Conc.	Blue 113
Amacid Cyanine G Conc.	Blue 116

Neutral Dyes

26. Because of their complex chemical structure and colloidal nature, neutral dyes are of excellent fastness to wet treatments such as washing and scouring, to treatments which require the application of alkalis. Generally, Group C acid dyes exhibit all the good fastness properties of groups A and B, and in addition show improved fastness properties to light, alkaline perspiration, wet treatments, and crocking. The solubility of neutral dyes, however, is considerably less than that of the other dyes. Dissolving in boiling water causes precipitation of some neutral dyes, but boiling water never causes precipitation of the acid dyes in groups A and B. Neutral dyes are dispersed in warm water of about 140 F with the aid of a wetting agent; this dispersion eliminates one cause of faulty dyeing when neutral dyes are applied to wool. Neutral dyes find use in the dyeing of men's suitings and shirtings, bathing suits, knitting yarns, buntings, and the like. Some typical milling or neutral dyes are listed in Table 3.

Practical Neutral Dyeing

27. For the successful application of Group C acid dyes, rigid control of pH is necessary. This is especially true when dyeing piece goods.

The bath is prepared with 2% to 5% ammonium sulfate, and 0.5% to 2.0% ammonia of 26 deg Baumé; the goods are then allowed to circulate in this medium for a few minutes. The dyestuff, previously dispersed in warm water, is next added. The dye bath is slowly raised to the boil in 1 hr to 1½ hr, and boiling is continued until exhaustion is obtained, usually after 1 hr to 2 hr. The correct amount of ammonia to be employed is determined by the acidity of the material as received for dyeing. The initial pH of the dye bath is adjusted to about 7.5, which is followed by a gradual decline to acidity during the dyeing period.

In stock or package dyeing, satisfactory results are obtained with the pH adjusted to neutral or slightly acid. Many times, particularly with closed dyeing systems, the use of acetic acid is necessary for complete exhaustion.

28. Whereas ammonium sulfate comes in the form of a white crystalline solid,

TABLE 4

VERSATILE DYES

Dyestuff	C. I. Name
	ACID
Supramine Yellow 3GLA	Yellow 29
Fast Red A	Red 88
Formyl Violet S4BA	Violet 17
Alizarine Irisol RD	Violet 43
Patent Blue AF Ex. Conc.	Blue 7
Cyananthrol RXO	Blue 47
Alkali Fast Green 10G	Green 22

ammonium acetate is prepared in solution as follows: One gallon of ammonia at 26 deg Baumé is diluted with 4 gal of water and added to $3\frac{1}{4}$ gal of acetic acid of 28% strength. This ammonium acetate mixture is adjusted until it is slightly alkaline, 1 gal being equivalent to $1\frac{1}{4}$ lb of ammonium acetate. The dye bath is prepared with 2% to 5% ammonium acetate and applied in the same way as ammonium sulfate.

A high-temperature method for the application of Group C acid dyes is sometimes used. Essentially, the method consists in entering the material into the dye bath as near the boiling point as possible. The dyeing assistants are 1% ammonium sulfate and 0.5% to 1.0% ammonia. The practicability of such a procedure is limited, its success being governed by the type of dyeing equipment used, such as the rotary or pedal type of dyeing machine, to be discussed later.

When diammonium phosphate is employed, the dye bath is prepared with amounts of 2% to 5% of the compound. Diammonium phosphate, which comes as a white crystalline solid, is readily soluble in cold water. Its function as a dyeing assistant with neutral dyes is similar to that of ammonium sulfate and ammonium acetate. With some neutral dyes, however, acetic acid may be necessary to obtain complete exhaustion.

Versatile Dyes

29. A small number of the level-dyeing acid dyes, such as those listed in Table 4, can be applied with good dyeing results by all three methods of acid dyeing. There are also a small number of acetic acid dyes in Group B that give equally good results when applied by the neutral dyeing method.

Shade Matching

30. Very often in dyeing it is necessary to add small amounts of dye as the dyeing progresses. This is done in order that an acceptable match may be obtained between the standard and the material being dyed. When the dye is added, the dye bath is already at the boil, and certain precautions in the selection of dyestuffs are necessary to prevent further dye additions from resulting in uneven color. Level-dyeing acid dyes are the simplest to add, with leveling results

obtained on continued boiling. Group B acid dyes produce satisfactory results when added to dye baths containing either Group B or Group C dyeing assistants. The addition of Group C acid dyes invariably produces unlevel and streaky dyeings, and these dyes should not be added for matching purposes. Only Group A and Group B acid dyes should be used for shade-matching purposes when the matching is done at or near the boil.

Chrome Dyes

Chemistry of Chrome Dyes

31. Chrome dyes, or mordant acid dyes as they are sometimes called, are applied to wool in conjunction with a metal mordant. Chromium compounds are the most important of the metal mordants, being used almost exclusively as the mordanting agent. Chemically, chrome dyes are similar to the acid dyes. The majority of these dyes are the sodium salts of color acids, and are members of the azo class ($N = N$). Other groups of importance are the anthraquinone, triphenylmethane, and the nitroso, or quinone $=$ oxime.

An important characteristic of the chrome dyes is the presence of one or more hydroxyl (OH) auxochrome groups in the dye structure. The hydroxyl radical is responsible for the inherent property of fastness to the wet treatments of washing, scouring, and fulling that makes the chrome dyes outstanding. Other auxochrome groups that may be present are the sulfonic, SO_3H, carboxyl, COOH, and amine, NH_2.

Generally, chrome dyes, except for some chrome yellows, are colloidal dyes having molecular weights varying from 242 to 1080. They form large colloidal aggregates of much the same order as the neutral or milling dyes. In addition, further aggregation of chrome dyes is promoted by the presence of the metal mordants, necessitating considerable caution in the application of these dyes to wool.

Metal Mordants

32. The introduction of metal hydroxides into chrome dyes produces a stable dye complex, or color lake, of improved fastness to washing, fulling, and light. In a color lake, tin imparts the highest brilliance; and aluminum, chromium, copper, and iron impart brilliance of a decreasing order. These metal mordants further bring about improved fastness to light when they are employed in the reverse order, with iron producing the maximum improvement and the other metals, improvement of a decreasing order. Since chromium occupies the middle position of the metals listed, it imparts both adequate fastness to light and adequate brilliance of color to chrome dyes, and it is usually selected as the mordanting agent.

Usually the introduction of various metal mordants into chrome dyes will

bring about complete changes of shade. The resulting dyes are known as poly-. chromatic. Certain dyes, however, produce only one shade, irrespective of the metal introduced; these are known as monochromatic.

Use of Chrome Dyes

33. Although chrome dyes provide a complete range of shades, they lack the brilliance of color that is characteristic of acid dyes. Consequently, many acid-dyed shades are not reproducible with chrome dyes. However, a satisfactory degree of brilliance in color is attainable with chrome-dyed materials when the chrome dyes are combined and used with milling or neutral dyes. This method of obtaining brilliance is possible because many of the chrome dyes exhibit level-dyeing properties similar to those of the milling or neutral dyes.

Generally, chrome dyes have level-dyeing properties which are equivalent to the properties of the acid dyes of groups B and C. In other respects, chrome dyes are superior to acid dyes, having improved fastness to light and excellent fastness to washing, scouring, fulling, alkaline perspiration, crocking or rubbing, hot pressing, decating, and dry cleaning. Some chrome dyes, such as Diamond Black PV, C.I. Mordant Black 9, Alizarine Blue Black B, C.I. Mordant Black 13, and Eriochrome Black T, C.I. Mordant Black 11, show increased stability during finishing processes such as potting or crabbing.

Most chrome dyes are of an inferior fastness to carbonizing, a process that may cause a complete change in shade. There are available, however, a few chrome dyes which show satisfactory fastness to carbonizing when dyed by the metachrome method. The dyeing of carbonized piece goods with chrome dyes, when preceded by neutralizing, will usually reveal carbonizing faults. Therefore, the utmost care for uniform acid distribution, and for baking of the material during carbonizing, will be necessary.

When extreme fastness properties are desired in dyeing men's-wear suitings, overcoatings, and shirtings, chrome dyes are of primary importance. They also find use in the dyeing of carpet wools, upholstery materials, and knitting yarns for sweater and stocking use.

Mordanting Agents

34. Sodium bichromate containing two waters of crystallization, $Na_2Cr_2O_7 \cdot 2H_2O$, is generally employed by the majority of mills as the mordanting agent. Potassium bichromate is equally suitable but, because of its slightly higher price and its lower solubility, it has not been adopted to any great extent for commercial use. The metal chromium has an increased affinity for wool, and it chemically combines with the basic side chains of the wool. Chromium is a hexavalent metal, however, and the increased fastness properties of the color lake to washing, fulling, and light are not realized unless chromium is in its trivalent form. This state is brought about by a boiling temperature, with the assistance of a reducing

acid agent such as lactic, acetic, formic, oxalic, or tartaric acid or potassium acid tartrate. These reducing agents aid in the reduction of sodium bichromate to chromic oxide or hydroxide.

Methods of Applying Chrome Dyes

35. Chrome dyes are applied to wool by one of the following methods: 1) the bottom-chrome, or chrome-mordant, method; 2) the top-chrome, or afterchrome, method; or 3) the chromate, or metachrome, method.

Choice of the method of applying a chrome dye is governed by its degree of levelness. For convenience in assigning ratings, Grade 5 designates excellent levelness and Grade 1 designates poor levelness. For satisfatory results, chrome dyes of level-dyeing grades 1 and 2 are generally applied by the bottom-chrome or chromate methods. Dyes of improved levelness, grades 3 to 5, are applied by the top-chrome method.

If it is desired, some of the level-dyeing chrome dyes can be applied by the bottom-chrome method. These dyes require the use of acetic acid for complete exhaustion, particularly medium-to-dark shades such as Eriochrome Flavine A, C.I. Mordant Yellow 5, or Alizarine Red S, C.I. Mordant Red 3. With certain chrome dyes, complete chromation can be obtained only by one method of application. This is true of Acid Anthracene Brown PG, C.I. Mordant Brown 40, Eriochrome Black T, C.I. Mordant Black 11, and Diamond Black PV, C.I. Mordant Black 9, all of which are best dyed by the top-chrome method. For these dyes the bottom-chrome or chromate methods would yield inferior color values and poor fastness properties. On the other hand, Anthracene Chromate Brown EB, C.I. Mordant Brown 1, is best dyed by the chromate method. Most chrome dyes that can be applied to wool by the bottom-chrome or chromate methods can also be applied satisfactorily to wool stock or slubbing by the top-chrome methods.

Bottom-Chrome Method

36. The bottom-chrome method requires, as the initial step, the reduction of the sodium bichromate to chromic oxide on the wool fiber. This is followed by the application of the chrome dyes in a separate bath for the formation of the color lake. The process consists in boiling the wool with a solution of sodium bichromate and cream of tartar (potassium acid tartrate), or its equivalent commercial product of half-refined tartar, for a length of time sufficient to effect reduction. Potassium acid tartrate is bought as a crystalline substance, the color of which varies from gray to brown. Since it is not easily soluble in water, it provides for a gradual and uniform reduction of the bichrome. Half-refined tartar, or argol, an impure form of tartar which is obtained from grapes as a deposit from wine fermentation, is generally employed as the mordanting agent. The reduction of the bichromate is indicated by a change of shade from yellow-orange to greenish yellow.

The decreased acidity of half-refined tartar during chroming is an advantage, especially when employing poor level-dyeing chrome dyes, because this type of tartar does not interfere to any great extent with the functioning of the ensuing dyeing assistants. Other reducing acid agents, such as lactic, acetic, formic, sulfuric, and tartaric acid, are also satisfactory. Owing to their increased acidity, however, they tend to induce a more rapid exhaustion of the bichromate, resulting in uneven reduction and consequently uneven dyeing. For satisfactory dyeing results, a more careful control of the time-temperature cycle is necessary when employing mordanting agents of increased acidity; also necessary is the use of the more level chrome dyes. If there is not careful control of the time-temperature cycle, the acidity must be controlled by neutralization before proceeding with the dyeing.

It is imperative that chrome-mordanted material be protected from direct sunlight. If it is not, a decomposition of the chrome mordant will occur, promoting uneven chromation and consequently uneven dyeing.

37. The bottom-chrome method is employed mainly for the dyeing of piece goods. Its two-bath process, however, makes it a time-consuming operation which is not in accord with the high-speed processing methods that are favored today in the textile industry. Nevertheless, in spite of this disadvantage, the bottom-chrome method is still employed for dyeing densely constructed worsted fabrics. It is especially suited to medium and dark shades because in these shades it produces excellent penetration, solidity of color, and fastness properties — qualities that are difficult to duplicate by the top-chrome or metachrome methods. Another advantage from the dyer's standpoint is the comparative ease with which the sample is matched, since the process in color development can be observed, and dyestuff additions made, when necessary.

38. The bottom-chrome mordanting bath is prepared with 1% to 2% sodium bichromate and 3% half-refined tartar. Enter the material, raise the chroming bath to the boil in 30 to 45 min, and boil for 1 hr to 1½ hr. Reducing agents other than tartar are used in amounts of 1% to 2% formic acid, 1% to 2% oxalic acid, or 2% to 4% lactic acid. As previously stated, these reducing agents require careful control, and the use of the more level chrome dyes, for satisfactory dyeing results.

After mordanting, the material is washed and the bath prepared for the ensuing dyeing operation. The bath is made slightly alkaline by adding one of the following dyeing assistants: 1) 2% to 5% ammonium sulfate with 0.5% to 2% ammonia; 2) 2% to 5% ammonium acetate; or 3) 2% to 5% diammonium phosphate.

The material is allowed to circulate in the prepared bath for a few minutes and then the dyestuff, previously dispersed with water, is added. As with neutral

dyes, the dissolving of chrome dyes with boiling water is avoided in order to prevent precipitation. The dye bath is then slowly raised to the boil in 1 hr to 1½ hr, and boiling continued for 2 to 3 hr. The time needed to raise the temperature of the dye bath to the boil depends on the type, weight, and condition of the material being dyed. Additional ammonium sulfate or acetic acid may be necessary to effect complete exhaustion of the dye bath. The exact amounts to be used must be determined by experimentation.

Top-Chrome Method

39. The top-chrome method for the application of chrome dyes takes considerably less time than the bottom-chrome method. Essentially, the process is the reverse in application of the bottom-chrome method. There is a saving in dyeing time because the chrome dyes are applied as the base, being followed in the same bath by the addition of the sodium bichromate. With this method there must be complete exhaustion of the dye bath; otherwise, streaky color and precipitation of the chrome dye complex will result. These conditions result from the aggregation of the chrome dye complex in the solution, rather than on the wool fiber.

After exhaustion, the dye bath is cooled to 180 F and the bichromate added. The temperature is then raised to the boil and boiling continued for the length of time necessary to achieve chromation. If complete exhaustion of the dye bath is not attained, the excess dye is removed by washing; chroming is then commenced in a fresh bath. The amount of bichromate needed for complete color-lake formation varies with the dyestuff. Generally, one-quarter to one-half as much chrome as dye is considered an ample amount. For many dye formulas, particularly for light shades, this amount of chrome is more than enough. Any surplus tends to dull the shade, and this dulling becomes a hindrance to shade matching.

Sodium bichrome in amounts no less than 0.375%, based on the weight of the material, will produce satisfactory results for light-to-medium shades; amounts of 1% are used for dark shades. For practical dyeings, satisfactory results are obtained with 0.125% to 0.3% chrome for 0.25% of dye, or less, based on the weight of the wool. For amounts of dye greater than 0.25%, the amount of bichromate should be one-quarter of the amount of dye, but greater than the quantity of chrome used for 0.25% of dye. Smaller amounts of bichromate will invariably result in inferior properties of fastness to wet treatments.

40. Top-chrome dyes are considered to be the level-dyeing chrome dyes, grades 3 to 5. They are therefore applied with the use of Glauber's salt for leveling, and of acetic acid for exhausting. Medium-to-dark shades require formic acid for complete exhaustion. Generally, chrome black, navy, and blue shades are dyed by the top-chrome method. The navy component is usually Acid Chrome

Blue 3BA, also known as chromotrope. Chromotrope is an acid dye (C.I. Acid Red 12) and can be used as such if desired; it produces a red shade. With the addition of chrome, however, it is gradually converted to a navy shade on continued boiling. The fastness properties of the chromotropes, although improved tremendously for wet treatments by the formation of the chrome dye complex, are nevertheless inferior to those of most afterchrome dyes.

The main disadvantage of the top-chrome method is the difficulty is presents to the dyer in the matter of shade matching. Any deviation of a dye formula from standard during the dyeing period cannot be observed or coped with until after the chroming operation. After the addition of the sodium bichromate, a pronounced change of shade results with most chrome dyes. Also, a part of the yellowing component in the shade is taken from the bichromate. Usually there is a period of 3 to 4 hr of dyeing time before any adjustments can be made for shade matching.

41. The top-chrome method is employed principally for stock dyeing, and to a less extent for piece goods. It is employed, however, for piece goods in black and navy shades, and for piece goods containing decoration yarns of silk or nylon. In the dyeing of decoration-yarn fabrics, the top-chrome method helps to maintain clarity and brightness of shade in the yarns.

Chemically, silk is a protein fiber similar to wool. The difference between them is that silk does not contain cross linkages in its molecular structure. Silk has an affinity for, and is generally dyed by, the same class of dyes as wool. However, when dyed with the afterchrome dyes, silk does not have this affinity for wool dyes, and any slight degree of staining can be removed by the use of acetic acid. Nylon, a synthetic polymer, is left clear and bright in shade if dyed with selected afterchrome dyes.

42. The bath for top-chrome dyeing is prepared with 10% Glauber's salt and 2% to 4% ammonium sulfate. Enter the material and allow it to circulate for a few minutes to obtain uniform distribution. The dyestuff, previously dissolved in water, is then added. The dye bath is slowly raised to the boil in 1 hr to $1\frac{1}{2}$ hr. After boiling $\frac{1}{2}$ hr, exhaust the bath with two or three 1% portions of acetic acid (56% strength) at intervals of $\frac{1}{2}$ hr.

If complete exhaustion of the dye bath cannot be attained, exhaust further with 2% formic acid. The dye bath is then cooled to 180 F, and the sodium bichromate added. The temperature is again raised to the boil and boiling continued for $\frac{3}{4}$ hr to $1\frac{1}{4}$ hr. The amount of chrome necessary varies with the type and amount of dye present. Generally, amounts of one-quarter to one-half as much chrome as dye are satisfactory. When shade development is slow, it is usually an indication that longer boiling periods are necessary, or that additional bichromate is needed to complete the development of the chrome dye complex.

Metachrome Method

43. The metachrome, or chromate, method is the simplest of all three methods of chrome dye application. Yet the dyeing results can be unsatisfactory, because the over-all dyeing appearance may show poor penetration due to nonuniform distribution of the chrome dye complex within the pores of the wool fiber. Rapid development of the chrome dye union will cause surface fiber dyeing, which results in poor crocking or rubbing properties. Poor crocking properties are not uncommon when the dyestuff and the method of application have not been chosen with care.

Since its introduction in 1900, the metachrome method has been extensively adopted wherever it will give satisfactory results. The metachrome method, when compared to other methods, represents a substantial saving in dyeing time. Essentially, the method consists in the application of both the chrome dye and the bichromate to wool from the same bath, as one single operation. Shade matching by this method is rather simple, since the progress of shade development can be easily followed and color additions made accordingly.

44. In metachrome dyeing the main thing is to prevent the formation of the chrome dye complex in solution. Otherwise there will be increasing colloidal aggregation, causing poor penetration and unsatisfactory dyeings. With proper pH control, however, satisfactory dyeing results are attainable.

Sodium bichromate increases in its affinity for wool with a rise in acidity. Consequently, chrome dyes that have a marked affinity for wool near the neutral point — the level-dyeing grades 1 and 2 — are adaptable to the metachrome method. The mordant is taken up by the wool fiber independently of the dye, and the chrome dye union is formed on the wool fiber. Color application by the metachrome method is achieved by the use of dyeing assistants. These maintain a slight initial alkaline pH of about 7.5. When the temperature is increased to 212 F, they become neutral; and finally, on continued boiling they change to slightly acid. Such dyeing assistants as ammonium sulfate and ammonia, ammonium acetate made alkaline, and diammonium phosphate are satisfactory. These assistants repel dye affinity at low temperatures and facilitate swelling of the wool, thus aiding in uniform diffusion of the dyestuff. They also assist exhaustion, owing to the acid liberated from the development of ammonia. This release of acid is in turn followed by the reduction of the bichromate to chromic oxide and by the formation of the chrome dye complex. Chrome dyes that show the least change in shade in the presence of bichromate are an advantage in obtaining uniform shades in metachrome dyeings.

45. Metachrome mordants are marketed under various trade names for chromate dyeing. These consist of a mixture of one part potassium chromate and two parts ammonium sulfate. It has been shown that, with the use of such meta-

chrome mordants, the chromium combines with the wool as chromic oxide, which is liberated from the potassium chromate by hydrolysis. A rise in alkalinity is prevented by the liberation of sulfuric acid from the ammonium sulfate, because of the evolution of the ammonia. The solution remains slightly acid, and some bichromate is formed. This bichromate is also reduced to chromic oxide by hydrolysis.

46. In spite of all precautions taken for the satisfactory application of chrome dyes by the metachrome method, dyeings of poor quality on tightly-woven worsted piece goods are often found, especially with medium-to-dark shades. This condition is due to increased aggregation with increasing dye concentration. Equivalent shades by the bottom-chrome method are far superior, with excellent dyeings, unlike the poorly penetrated and streaky dyeings of the metachrome method. Light shades, however, are dyed by the metachrome method with highly satisfactory results. The use, as a penetrant, of a small amount of highly sulfonated vegetable oil aids to some extent in the diffusion of the dye within the wool pores.

For stock and top dyeing, the metachrome method gives satisfactory dyeing results, regardless of the depth of the shade. However, the use of acetic acid is necessary for complete exhaustion and color lake formation. Very often the slight unevenness of color that may appear in stock or top dyeing can be attributed to the dyeing equipment employed and to the condition of the wool stock or top. However, small variations in color are not too important, because further uniformity is obtained by the subsequent operations such as carding, spinning, and drafting.

47. Any one of the following four groups of dyeing assistants may be employed for chromate dyeings: 1) 2% to 5% ammonium sulfate, 0.5% to 2% ammonia, 1% sulfonated vegetable oil, and 0.125% to 1% chrome. 2) 2% to 5% ammonium acetate (made alkaline), 1% sulfonated vegetable oil, and 0.125% to 1% chrome. 3) 2% to 5% diammonium phosphate, 1% sulfonated vegetable oil, and 0.125% to 1% chrome. 4) 2% to 6% metachrome mordant, 4% to 6% ammonium sulfate, and 1% sulfonated vegetable oil.

The material is circulated for a few minutes with the dyeing assistants to make sure of uniform distribution. This is followed by the addition of the bichromate. The dyestuff, previously dispersed in warm water, is then added. The dye bath is slowly raised to the boil in 1 hr to $1\frac{1}{2}$ hr and the boiling continued for 1 hr. Exhaustion of the dye bath may be accelerated by additional amounts of ammonium sulfate, about 2%, and by continued boiling.

Typical Chrome Dyes

48. Chrome dyes that are adaptable for use by the bottom-chrome or metachrome methods are listed in Table 5.

TABLE 5

BOTTOM-CHROME AND CHROMATE DYES

Dyestuff	C. I. Name
	MORDANT
Metachrome Red F Conc.	Red 19
Alizarine Orange 2GN	Orange 1
Superchrome Yellow GN	Yellow 3
Omega Chrome Green B	Green 9
Diamond Green SS	Green 11
Alizarine Navy Blue AT Ex. Conc.	Blue 10
Fast Mordant Blue B	Blue 13
Anthracene Chromate Brown EBA Ex. Conc.	Brown 1
Acid Anthracene Brown KE	Brown 15
Metomega Chrome Brown RLL	Brown 63
Erio Chrome Blue Black BC	Black 3
Alizarine Blue Black B	Black 13
Erio Chrome Blue Black RZ	Black 17

Chrome dyes which are satisfactory for use by the top-chrome method are listed in Table 6. The dyes in both of these tables are listed in the same manner as the dyes in previous tables.

Shade Matching

49. There are a great number of variations in wool dyeing, particularly with chrome dyes. Therefore it is often necessary to add a small amount of color during the progress of the dyeing so as to match as closely as possible the color of a given standard. The careful selection and addition of dyestuff is required for this purpose; otherwise faulty dyeings will result.

Chrome dyes with poor level-dyeing properties are entirely unsatisfactory for addition to a boiling dye bath. Top-chrome dyes with fair-to-good level-dyeing properties are better suited for obtaining final shade adjustments. Nevertheless, their use requires certain precautions, such as cooling the dye bath to as low as

TABLE 6

TOP-CHROME DYES

Dyestuff	C. I. Name
	MORDANT
Alizarine Yellow 2G Conc.	Yellow 1
Acid Alizarine Flavine RA	Yellow 8
Omega Chrome Yellow ME	Yellow 30
Chrome Fast Orange 3RLA	Orange 4
Alizarine Red S	Red 3
Erio Chrome Red B Conc.	Red 7
Erio Chrome Azurol BA Ex.	Blue 1
Erio Chrome Cyanine R	Blue 3
Acid Anthracene Brown PGA	Brown 40
Erio Chrome Black T Supra	Black 11

160 F to 190 F before addition, then raising the temperature to the boil, and boiling to obtain exhaustion. Some Group B acid dyes are also available for shade adjustments; these have an affinity for wool with level-dyeing results near the neutral point. Group B acid dyes, if used in small amounts, will not detract to any great extent from the fastness properties of the chrome dyeings.

Dyeing Tippy Wool

50. In wool dyeing with chrome dyes, the wool stock will often be one that dyes with both light and dark places in the same fiber. Such dyeings are indicative of tippy wool or damaged fibers, sometimes due to the action of sunlight on the wool, and sometimes due to the fact that the wool came from a certain region. Australian wools, for example, produce more pronounced variations than domestic wools. Damage to wool by sunlight is accompanied by increased swelling (due to a loss of scales), pronounced shrinkage, a loss in tensile strength, and a harsh hand.

Generally, with tippy wool, the top-chrome method leads to better level-dyeing results than the metachrome method. Nevertheless, two-tone effects or skittery dyeings are not entirely prevented by use of the top-chrome method. The reason is that, when certain dyestuffs are used, this condition is greatly pronounced, even though the dyestuffs may exhibit good level-dyeing properties. Recently there have been introduced several auxiliary products which produce level-dyeing results when employed with chrome dyes. Some of these are Antho-mine, Peregal TW, and Invadine, which are organic compounds, being essentially natural or synthetic fatty esters in combination with nitrogen compounds.

Metalized Dyes

Chemistry of Metalized Dyes

51. The metalized dyes fall into two classes: acid metalized dyes and neutral-dyeing metalized dyes. The acid metalized dyes contain one atom of metal for one molecule of dye and also one or more sulfonic acid groups. Mordant acid dyes are the acid azo dyes (o-hydroxyazo compounds), which contain metalizable groups such as hydroxyl, or pairs of hydroxyl and carboxyl, or hydroxyl and amino. The chromium metal, in its trivalent form, is mainly employed for intro-duction in the dye complex; it is joined to the azo group. Other metals, such as iron and cobalt, are also used but to a less extent than chromium.

It is believed that the chemical fixation of metalized dyes consists of two stages: 1) Because metalized dyes are azo dyes containing one or two sulfonic groups, there results a salt formation with the basic groups of the wool. 2) The chromium of the dye combines with other basic groups of the wool, thus further insolubilizing the formation of the dye complex with the wool.

Application of Acid Metalized Dyes

52. A simple one-bath process for dyeing is made possible by the use of acid metalized dyes. This represents a substantial saving in dyeing time, as compared to the bottom-chrome and top-chrome methods. The application of acid metalized dyes, however, requires a high percentage of sulfuric acid, 6% to 8% on the weight of the material, and sufficient boiling, usually 2 to 3 hr, to bring about levelness and exhaustion of the dye bath. A high percentage of acid and longer time are necessary because of the colloidal aggregation of acid metalized dyes, which are therefore dyes of poor level-dyeing properties, being grades 1 to 3. Smaller amounts of acid, or less boiling time, invariably result in undeveloped shades and faulty dyeing, especially for medium-to-dark shades.

The main disadvantage in the use of acid metalized dyes is considered to be slight fiber degradation, resulting in a loss of tensile strength. This degradation is caused by the prolonged boiling periods with increasing amounts of acid. As a means of counteracting the harmful effects produced by acid metalized dyes, there are available auxiliary products for dyeing, in the presence of which the amount of acid is decreased to 4% to 5%. These products are Palatine Fast Salt O solution, an ethylene oxide condensation product; Palatine Fast Salt N powder, an alkylarysulfonate; and similar products, such as Neolan Salt II, which promote leveling and exhaustion of the dye bath. With some acid metalized dyes, such as Palatine Fast Yellow ELN, C.I. Acid Yellow 54, difficulty is experienced in obtaining complete exhaustion with decreased acidity.

Piece goods containing decoration yarns of cotton, rayon, or acetate produce unusual effects when dyed with acid metalized dyes because the acid tenderizes the cellulose fibers during drying. The material may be neutralized after dyeing, at a low temperature. Neutralizing, however, results in a change of shade, making shade matching difficult. Therefore the use of acid metalized dyes is unsatisfactory for piece goods with decoration yarn effects.

53. Acid metalized dyes exhibit excellent fastness properties to such wet treatments as washing, scouring, and fulling, and to alkaline perspiration and sea water. Generally they are equivalent to most chrome dyes in fastness ratings. For light fastness, acid metalized dyes show excellent properties in self shades, but with certain combination mode shades they are somewhat inferior to chrome dyes. Acid metalized dyes, like chrome dyes, are also deficient in brilliance of color. Some shades, such as bright greens and blues and purples, are unattainable. This shortcoming is minimized by use of the Group A acid dyes interchangeably with acid metalized dyes. Shade adjustments with acid metalized dyes are comparatively simple, provided that sufficient boiling time is allowed to promote leveling of the color additions. Acid metalized dyes find considerable use in the dyeing of woolen and worsted piece goods, slubbing, raw stock for carpet wools, and yarns for bathing suits, sweaters, and stockings.

TABLE 7

ACID METALIZED DYES

Dyestuff	C. I. Name
	ACID
Palatine Fast Yellow ELNA	Yellow 54
Gycolan Yellow GRL Conc.	Yellow 99
Neolan Orange G	Orange 74
Vitrolan Orange R	Orange 76
Vitrolan Red GRE	Red 183
Neolan Pink B	Red 191
Gycolan Bordeaux RL	Red 194
Palatine Fast Violet 3RNA	Violet 56
Chromolan Blue NGG	Blue 158
Vitrolan Green BL	Green 12
Neolan Black WA Ex. Conc.	Black 52

54. The bath for acid metalized dyes is prepared with 6% to 8% sulfuric acid, depending on the desired depth of shade. The dyestuff, previously dissolved in boiling water, is then added to the dye bath. The temperature is raised to the boil. in 40 min. Boiling is continued for 2 to 3 hr, or until levelness is obtained with the material being dyed.

Carbonized materials can be dyed directly with the sulfuric acid contained in the material. Dark shades require additional amounts of acid, or a total amount equivalent to 8% sulfuric acid. As previously stated, the amount of acid may be reduced to 4% or 5% by the use of 3% Palatine Fast Salt O or equivalent products.

Typical Acid Metalized Dyes

55. Some characteristic acid metalized dyes are listed in Table 7 by their prototype name and number.

It should be noted that Neolan Black WA, C.I. Acid Black 52, requires a special method of application. The dye bath is prepared with 1.5% sulfuric acid. The temperature is raised to the boil in 30 min and the boil continued for 30 min. Then, with the steam shut off, 3% sulfuric acid is added and boiling continued for an additional 30 min. This procedure is repeated with another addition of 3% sulfuric acid, after which boiling is continued for $\frac{1}{2}$ hr to 1 hr.

Neutral-Dyeing Metalized Dyes

56. The neutral-dyeing metalized dyes are a completely new range of neutral-dyeing colors for wool and for nylon. The light and wet fastness properties of these dyes on wool are superior to those obtained from the use of common neutral-dyeing acid types, and they approach the fastness of chrome dyes. Two outstanding advantages of neutral metalized dyes on wool are that they exhibit inherently good fastness without chroming, and that they can be applied from

neutral dye baths. This second property is of exceptional value as a means of reducing the fiber degradation usually associated with the acid exhaustion of dyes for wool.

Neutral metalized dyes are best applied to wool from neutral dye baths or with the addition of 3% to 5% ammonium acetate, or of an equal amount of diammonium phosphate, at temperatures from 180 F to 212 F. The dye bath should be started cold and raised to the required temperature over a period of 45 min or more. In common with the neutral-dyeing acid types, the neutral metalized dyes do not transfer too well on wool, but under proper conditions of application very level dyeings are obtainable even on piece goods. Material to be dyed must be neutral or faintly alkaline, as material on the acid side results in too rapid exhaustion and corresponding unlevel dyeings.

There are a number of nonionic compounds being marketed that are of value as retarding agents for the dyeing of neutral metalized dyes. The main function of such compounds is to slow down exhaustion, which is a contributing factor toward greater levelness. Typical compounds are Capracyl Leveling Salt (Du Pont), Irgasol DA (Geigy), and Cibalan Salt S (Ciba).

Application of Neutral-Dyeing Metalized Dyes

57. There are two accepted methods of applying neutral-dyeing metalized dyes to all forms of wool, but especially to yarn and piece goods.

With the first method, the bath is set with 0.5% to 1% of the leveling agent, 5% ammonium acetate, and 1% ammonium hydroxide, and run for 10 min. The dye is then added and the temperature gradually raised to 180 F. The temperature is held at 180 F for 15 to 30 min, after which it is raised to the boil and dyeing carried out for 45 min before sampling.

The second method is to set the bath with 20% Glauber's salt, 1.5% of the

TABLE 8

NEUTRAL PREMETALIZED DYES

Dyestuff	C. I. Name
	ACID
Capracyl Yellow GW	Yellow 124
Cibalan Yellow FGL	Yellow 128
Capracyl Yellow 3RD	Orange 64
Lanamid Orange 2RL Conc.	Orange 85
Irgalan Orange RL	Orange 86
Nyalan Red NB	Red 182
Cibalan Bordeaux GRL	Red 213
Supralan Red BB	Red 273
Lanamid Violet DL	Violet 78
Supralan Blue NB	Blue 179
Irgalan Brown 2RL	Brown 45
Cibalan Olive 3BL	Green 70
Isolan Black GL	Black 138

leveling agent, and 4% acetic acid of 56% strength, and to run for 10 min. The dye is then added and the bath raised to the boil in 45 to 60 min. Dyeing is then carried out for 1 hr before sampling.

The second method provides dyeings with levelness superior to that from the first method. It also allows color additions to be made at the boil. However, the specified amounts of Glauber's salt and leveling agent are critically important and must be followed closely.

Some typical neutral premetalized dyes are listed in Table 8.

Natural Colors

Logwood

58. Of all the natural coloring matter, logwood alone has met the challenge of the synthetic dyes. Its use, however, is limited principally to rich blue-black shades. Logwood provides excellent fastness to scouring and fulling, but its light fastness is inferior to that of synthetic blacks. Use is made of logwood in dyeing felts.

The actual coloring matter of logwood is known as hematin. It is obtained as the oxidized extract from logwood. Overoxidized hematin, a brown resinous substance, has no value as a dye. The method of applying logwood depends upon the extent of its oxidation.

Methods of Applying Logwood

59. One method of applying logwood is as follows: Prepare a bath with 6 lb of unoxidized logwood crystals in 100 gal of water. The logwood must be previously dissolved with boiling water. Raise the temperature in 30 min to 200 F and maintain this temperature for 30 to 40 min. Wash thoroughly and then afterchrome with bichromate — 4 oz to each 10 gal of water. Raise the temperature again to 200 F and maintain this for 30 min. Add $2\frac{1}{2}\%$ to 5% acetic acid, based on the weight of the material, to the chroming bath to assist in the shade development.

With another method of application, the wool is mordanted with 1% bichromate and 2% formic acid. Raise the temperature to the boil, and boil 1 hr to $1\frac{1}{2}$ hr. Wash thoroughly. The dye bath is prepared with 20% to 30% hematin paste, or with 10% to 15% hematin crystals. Raise the temperature to the boil in 30 min, boil 1 hr to $1\frac{1}{2}$ hr, and wash. For shades of jet black, 3% fustic crystals is added with the hematin. Fustic, a natural yellow coloring matter, is obtained from trees.

Indigo

Natural Indigo

60. The use of indigo for wool dyeing is a long one. Indigo was employed in

Asiatic countries long before the Christian era, and later on the European conti-
nent. The indigo plant was grown principally in India.

The plant source from which natural indigo was obtained is known as *Indi-
gofera*, indigo being present in the form of a glucoside called indican. Indigo was
extracted from the plant leaves by a fermentation process whereby it decomposed
to its soluble compound of indoxyl, and thence to insoluble indigo by oxidation.
Natural indigo was rendered soluble for wool dyeing by a reduction fermentation
vat process which involved the use of wood, bran, and lime.

Synthetic Indigo

61. Increasing demands for indigo for cotton and wool dyeing led to the
preparation of synthetic indigo in 1880. As such, indigo is commercially available
in a paste form of 20% strength.

Synthetic indigo is soluble only in an alkaline medium. When synthetic indigo
is dissolved in an alkaline medium, it is known as the leuco compound of indigo,
or indigo white.

Solubility of indigo is caused by inhibiting oxidation by means of a reducing
agent such as sodium hydrosulfite, $Na_2S_2O_4$. On oxidation, as in washing and
airing, the leuco indigo reverts to its insoluble compound of indigo.

62. Indigo produces blue-to-navy shades of excellent fastness to washing and
light. They are of greater fastness when applied to wool than when applied to
cotton. Indigo is precipitated on the wool fiber in the form of crystallites, the
leuco indigo being molecularly dispersed, and followed by colloidal aggregation
on being oxidized to indigo.

An alkaline medium is necessary to make reduced indigo soluble. Caustic soda
is generally employed for this purpose. The alkalinity of caustic soda has no
harmful effect on cotton; with wool fibers, however, considerable degradation
results from the use of caustic alkalis. Rigid controls of temperature and concen-
trations are therefore necessary when using caustic soda in order to retard loss
in tensile strength.

As a means of restraining fiber degradation, the hydrosulfite ammonia vat
method was developed. This method makes use of glue as a protective colloid for
the wool fiber. Although ammonia provides for the solubility of the indigo by
this method, it is so weakly alkaline that complete solubility of the indigo is not
accomplished. The use of a small amount of caustic soda will afford greater
solubility with improved dyeing results. Precipitation of the indigo is still re-
strained, since the glue, acting as a protective colloid, maintains the indigo in
suspension and dyeing proceeds normally.

Application of Indigo

63. The following is a typical indigo vat, prepared for a volume of 600 gal:
Take 25 lb of ammonia (28% strength) and 1½ to 3 lb of sodium hydrosulfite.

Stir well and add 2 lb of dissolved animal glue and 15 lb of indigo paste. The color of the vat should be greenish yellow, and the vat should be free of sediment. Reduce it at 120 F for 20 min. Enter the wool previously wet out, thus minimizing the introduction of oxygen into the dye vat, and dye it for 20 to 30 min. Squeeze, oxidize, scour, and rinse. Scouring after dyeing is necessary to remove loosely held indigo, which would result in poor crocking or rubbing properties.

To obtain indigo dyeings of increased depth, the dyeing process is repeated. Further increments in shade are not possible without inferior crocking results; consequently added depth of shades is obtained by topping in a fresh bath. The top-chrome method employs such chrome dyes as Eriochrome Red B, Sulphon Cyanine 5R Ex, Alizarine Blue Black B, Eriochrome Blue Black B, and Eriochrome Blue Black R. Another form of indigo application is obtained with an Alizarine Red S on a chrome-mordant bottom, topped with indigo, producing indigo shades of a red cast.

64. With the introduction of synthetic coal-tar dyes there was a gradual decline in the use of indigo for wool dyeing. The principal drawbacks of indigo are 1) the excessive care necessary in its application and 2) contamination of the machinery, which makes it difficult to run light shades without staining. However, in view of its unique color characteristic, that is, navy shades rich in bloom when viewed overhand, indigo has been able to maintain some of its popularity. Similar navy shades produced with chrome dyes show decidedly red shades when viewed in artificial light, whereas indigo remains unchanged. For this reason, and more so for its excellent fastness properties, indigo remains unchallenged for the dyeing of wool for hard use as, for instance, in uniform material for the United States Navy.

Continuous Dyeing

65. As a result of the increased demands made by the United States Navy during World War II, continuous methods were developed for the dyeing of raw stock and piece goods with indigo. One continuous process for raw stock dyeing makes use of an eight-bowl scouring train as the dyeing machine. Principally, this continuous method is operated in the following sequence: wet out, enter in indigo vat, squeeze, oxidize, enter in indigo vat, squeeze, oxidize, and rinse twice. The first indigo vat is responsible for 60% of the color deposit on the wool fibers; 40% is obtained from immersion in the second indigo vat. The stock vat solution is prepared with caustic soda, sodium hydrosulfite, soda ash, and glue, the concentrations of which are maintained at constant levels throughout the dyeing period. Continuous circulation in the dyeing system is also maintained.

Du Pont Continuous Process

66. Except for the method described in the preceding article, practically all wool raw stock dyeing prior to 1953 was carried out by batch methods. Early in

1953 Du Pont introduced to the carpet trade a continuous process for dyeing wool raw stock using the last bowl of the wool scouring train. With this method scouring and dyeing could be carried out in one operation. It naturally suited the carpet industry, since large lots, ranging from 15,000 to 30,000 lb, are usually dyed for any one shade. The advantage of the savings in steam, water, and labor resulted in the acceptance of this process for production dyeing by many carpet manufacturers. No large expenditures for new equipment were required. Yarns spun from stock dyed continuously were also substantially stronger than yarns spun from kettle-dyed stock.

In this process the dye bath is charged with a predetermined amount of dye and sufficient formic acid to obtain a pH of 4.0 to 4.5. The addition of wool, formic acid, and dyes is started and the dyeing is carried out, usually at a rate of about 1200 lb per hr. A production rate of 3,000 lb per hr can be attained if the wool feed is increased accordingly. Shades are matched during the dyeing operation by making any required adjustments in the dye feed. Exact shade control is dependent on the uniformity of the wool feed. When the wool and dye feeds are closely synchronized it is possible to obtain dye lots requiring no correction batches to bring the shade to standard. When wide fluctuations occur in the wool feed, the correction lots necessary to match the standard are usually as frequent as those required when using batch methods. Commercial experience has shown that most of the lots dyed by this process require no correction dyeings, and that the levelness is generally superior to that of kettle dyeing.

67. The dyes best suited to this process are the neutral metalized dyes, because of their outstanding light and wet fastness properties and rapid but even exhaustion properties. A full shade range, including the clear bright shades, is attained by using selected neutral-dyeing acid colors. The process is not limited to these dyes alone, but it can also be used with almost all acid or chrome dyes. Use of this method for dyed wool for apparel end uses is becoming very popular, as full shades of black, navy, and brown can also be applied by this method. These heavy shades are produced by extending the dyeing time from 1.5 to 6 min and adding three bowls for rinsing and chroming.

The continuous process is not only useful for dyeing wool, but the same dyes and this same process can also be employed for nylon staple. Rayon likewise has been dyed commercially with direct dyes by this process. The continuous process, therefore, is commercially practical.

Vat dyes cannot be applied economically to rayon in the open scouring bowl because of the large area of dye bath exposed to the atmosphere, resulting in an excessive consumption of sodium hydrosulfite. Du Pont introduced to the trade the Flowstock process to overcome this problem.

The Flowstock process utilizes water as the means of propelling the stock through an enclosed tube, allowing the continuous application of vat and sulfur

dyes to rayon and cotton. Wool and nylon can be also dyed in this equipment. When wool and nylon are dyed, large savings in steam over the scouring bowl can be realized.

Piece Goods Dyeing

68. Piece goods dyeing with indigo is not often done with conventional dyeing machinery. This is because oxidation takes place during the dyeing, owing to exposure of the piece goods while being carried over the reel. In England piece dyeing with indigo is accomplished with the Hawkins machine. Because of its limited capacity, however, the Hawkins machine has not gained favor in America.

A continuous process for the application of indigo to woolen flannel piece goods has been developed. Dyeing is effected by padding the cloth with the indigo vat, allowing for a 3-min immersion time. The cloth is then squeezed, and finally it is aired for 5 min to obtain oxidation. This sequence of operations is repeated to obtain depth of shade. Afterward the pieces are scoured to remove loosely deposited indigo.

69. Other vat dyes similar to indigo are those of the indigoid and thioindigoid class, which are available under the trade name Helindones. They are applied to wool at a pH range of 8.5 to 9.0 by a method using sodium hydrosulfite, ammonia, and glue which are employed in the amounts of 1% to 3% ammonia, 2% to 4% sodium hydrosulfite, and 2% glue. The temperature of the bath is raised to 120 F to 140 F, and maintained for 30 min. If exhaustion is not satisfactory, 2% to 4% ammonium sulfate is added. The range of dyes of this type that are now available is sufficient to produce a complete line of shades.

Anthraquinone Vat Dyes

70. The anthraquinone series of vat dyes are of prime importance for the dyeing of cotton and other cellulose fibers. They are known for their unexcelled fastness properties to light, washing, bleaching, and perspiration. When applied to wool they produce the same excellent properties, particularly a fastness to light which cannot be equaled with acid chrome dyes. Their use with wool, however, has met with considerable disfavor, because fiber degradation results from the use of sodium hydroxide, which is necessary for their complete solubility.

Anthraquinone vat dyes are generally applied within a pH range of 11.0 to 12.5, and at temperatures of 120 F to 160 F. Milder alkalis, such as ammonia, trisodium phosphate, and sodium carbonate, are incapable of effecting the complete solubility necessary for satisfactory dyeing. The use of protective colloids to restrain chemical degradation of the wool at a high pH and at elevated temperatures is wholly inadequate.

71. One modified method of applying the anthraquinone vat dyes to raw stock or worsted tops utilized low temperatures of 90 F to 110 F. Accordingly, vat dyes

which exhaust easily at low temperatures are used. Reduction of the vat dye is first obtained separately in one-tenth the volume of the dyeing liquor. The addition of 3 oz per gal of sodium hydroxide and of 3 oz per gal of sodium hydrosulfite is necessary. The temperature is kept at 140.F for 15 min. The reduced vat dye is then added to the other nine-tenths of the dye bath, which contains 0.25 to 0.35 oz per gal of caustic soda and 0.25 to 0.50 oz per gal of sodium hydrosulfite.

Circulate the liquor for 15 min at 90 F. Next raise the temperature to 110 F, run for 20 min, and then add 2.0 to 6.0 oz of common salt per gallon to obtain exhaustion. A decrease in the alkalinity of the wool stock is brought about by the addition of 0.5 oz of sodium bicarbonate per gallon, converting the sodium hydroxide to sodium carbonate. This is followed by washing and oxidation with sodium perborate. Caustic soda is removed from wool with difficulty and so its conversion to sodium carbonate makes it easier to remove the alkali from the wool. Complete neutralization of the wool stock is assured by the addition of acetic acid to the oxidizing bath. Wool top dyed by this method produces dyeings of excellent fastness to light and washing, and shows only limited fiber degradation in comparison to metachrome dyeings.

The application of vat dyes to piece goods presents a more difficult problem. A constant check of the dye bath is necessary to prevent oxidation, which would otherwise insolubilize the leuco compound, resulting in dye aggregation and consequently poor dyeing. Anthraquinone vat dyes on wool piece goods likewise present production difficulties, as well as greater reductions in tensile strength, when applied with present methods and conventional piece-dyeing machines.

Indigosols

Chemistry of Indigosols

72. Indigosols are basically vat dyes which have been rendered water-soluble in the form of their leuco esters, and which are applied to wool from a neutral or acid bath. Their method of manufacture provides for the sulfation of indigo and other vat dyes of the indigoid and anthraquinone series, converting their hydroxyl derivations to an ester of sulfuric acid. As a result of this process, the excellent fastness properties of vat dyes have been made available to wool, without the danger of alkali fiber damage. The leuco esters have a greater affinity for wool than for cotton, but their affinity for both varies with the temperature. At low temperatures they have an affinity for cotton, whereas at boiling temperatures their affinity is directed to wool. Complete shade development of the leuco esters on wool is obtained by oxidation, which reconverts the soluble leuco esters to their original vat dye.

Use of Indigosols

73. Although the indigosols have been in use to a limited extent for a long

time, they are becoming more and more important because of the increasing demand for washable wool fabrics. Indigosols give excellent fastness properties to light, wet treatments, and bleaching. For these properties, which are needed in washable fabrics, acid and chrome dyes are not completely satisfactory. On the other hand, indigosols are expensive, and because of their low color value, dark shades could be obtained only at an exceedingly high cost.

Indigosols can be satisfactorily applied to raw stock, top, and yarns. On piece goods their application has been limited. Other leuco esters, similar to indigosols, are manufactured under the trade names of *Algosols, Du Pont* soluble vats, and *Calco* soluble vats.

Application of Indigosols

74. The dye bath is prepared with 2% to 10% ammonium sulfate and 10% Glauber's salt. Increased amounts of ammonium sulfate are employed for increased depth of shades, and also when alkalinity prevails in the material after scouring. The leuco ester, previously dissolved in warm water, is then added to the dye bath. Boiling of the leuco ester is not necessary for dissolving, and it should be avoided, thus preventing premature oxidation. Dyeing is started cold, or at 100 F, and the temperature is raised to the boil in 1 hr. Because a large percentage of the leuco ester exhausts at temperatures between 160 F and 200 F, considerable care should be exercised at those temperatures. Boiling is continued for $\frac{1}{2}$ hr to 1 hr, in which time exhaustion is obtained.

With increased depth of shade, a small amount of acetic acid may be necessary to effect complete exhaustion. The dye bath is rinsed and shade development is obtained by oxidation. The dye bath contains 13 oz of sulfuric acid for each 10 gal of liquor, to which is added 0.7% to 3% sodium bichromate and 1% to 3% ammonium sulfacyanide, calculated on the weight of the material and according to the depth of the shade. The temperature is raised to 185 F to 190 F in 30 min and maintained at that point for 30 min. The material is then washed and neutralized with sodium carbonate. The addition of the ammonium sulfocyanide prevents overoxidation of the leuco ester by forming a chrome complex; it also prevents dulling of the shade.

75. Indigosol O and OR require a slightly different method of application from that used with the leuco esters described, because a stronger acid is necessary to promote complete exhaustion. The dye bath is prepared with 10% to 20% Glauber's salt, 3% sulfuric acid, and 1% sodium hydrosulfite. The indigosol O or OR, previously dissolved with warm water and practically colorless, is then added to the dye bath. Sodium hydrosulfite is employed to restrain premature oxidation. The temperature is raised to the boil in 1 hr and boiling continued for 1 hr. The material is then washed. Color development is obtained in a fresh bath prepared with 1% to 2% sodium nitrite and 12% to 15% sulfuric acid; and the material is

treated for 1 hr at 140 F. Rinse and neutralize with 8% to 10% sodium carbonate at 140 F for 20 min and then wash.

To satisfy the increased demands of the Navy Department during World War II for indigo-dyed flannel, a satisfactory substitute was obtained with indigosol O, topped with chrome dyes to obtain greater depth of shade. For topping, the top-chrome method is employed with the chrome dyes that were indicated in describing the application of indigo.

As other demands and critical needs arise, the research laboratories of the dyestuff manufacturers will work overtime to develop new dyes for different purposes. In order to keep abreast with all the new developments, the dyeing and finishing technician should make it a habit to scan the trade literature for articles on new dyestuffs and new dyeing methods.

Union, or Blend, Dyeing

Problems of Union Dyeing

76. The dyeing of unions, or mixed fabrics containing two or more different types of fibers, presents to the dyer more difficult problems in every way than does the dyeing of fabrics containing only one type of fiber. For example, two or more dyes may have to be selected in order to produce multicolored cross dyeings, the selections being dependent upon the fibers in the blend. Then again it may be desired to achieve complete solidity of color. The principal fibers employed in blends with wool are cotton, rayon, acetate, and nylon. A knowledge of these fibers and the dyestuffs to be employed, particularly of the fastness properties of the dyestuffs, is necessary for the successful dyeing of materials containing blends of two or more different fibers.

The production of multicolored fancy fabrics or of solid shades becomes comparatively simple when the wool is dyed in the form of raw stock, worsted top, or yarn. A number of yarns, varying in color, may then be woven into a fabric. Similarly, cotton, rayon, and nylon can be dyed separately and then woven with wool fibers to produce many desired effects. Excellent fastness properties to light, washing, crocking, and perspiration are obtained for such fabrics when Group C acid or chrome dyes are used in dyeing the wool and nylon; and when vat sulfur, or direct cotton dyes, Group C, are used for the cotton and rayon. However, the production costs of fabrics woven from separately dyed yarns are higher than those of kettle-dyed piece goods. Piece dyeing has the further advantage that fabrics woven in advance can be dyed to any desired shade in accordance with the latest color fashion trends. Union piece-dyed materials are therefore of considerable importance to the trade.

Methods of Union Dyeing

77. Union dyeing of fabrics containing wool may be accomplished by any of

three methods. The method selected depends upon the fastness requirements and the amount of wool in the blend. The three methods are 1) the one-bath method, 2) the two-bath method and 3) the vat-dyed method.

The one-bath method is the most popular of the three methods and the one generally employed, because it represents a substantial saving in dyeing time. The dyeing of wool and cellulose fiber blends is accomplished from the same bath, which utilizes neutral acid dyes for the wool and direct cotton dyes for the cellulose fibers. However, the fastness properties to wet treatments are inferior, particularly for dark shades, and a high percentage of direct dyes is required. Shade matching is also very difficult when dyeing solid shades, because there must be a correct balance in dye-stuffs to obtain a uniform shade appearance among the different types of fibers present. Direct dyes employed for dyeing cellulose fibers have an increased affinity for wool with increasing temperatures, whereas, at low temperatures, many of the direct dyes have a negligible affinity for wool. Careful control, therefore, of the time-temperature dyeing variables is of primary importance in assisting shade development and adjustments.

78. The two-bath method of union dyeing is employed to a less extent than the one-bath method, because it requires longer dyeing periods. The wool and cellulose fibers are dyed to the desired shade from separate baths. The fastness properties of the wool fiber content are of improved quality when dyed with selected Group C acid dyes or with chrome dyes. If the wool is dyed with Group A or Group B acid dyes, it is necessary to use formic or acetic acid to retard loss in tensile strength of the cellulose fibers that results during drying. Shade matching by the two-bath method is easier: the wool is first dyed to standard, and then the cellulose fibers are adjusted to the shade from a separate bath. Temperatures of 120 F to 140 F are maintained to prevent staining of the wool when dyeing the cellulose fibers.

A further means to prevent staining of the wool is the use of retarding agents, which depress the affinity of direct dyes for animal fibers. These agents, which are mixtures of phenol and sulfur condensate products, are employed in amounts of 1% in the direct cotton dye bath. Further shade adjustments of the wool fibers may be made from the cotton dye bath with selected acid dyes having an affinity for wool at low temperatures.

The vat dye application to union material is generally employed for wool-cellulose blends in which the wool fiber content amounts to 20% or less. With vat dyes, excellent fastness properties are attained for cellulose and wool fibers.

Dyes for Wool-Cotton Blends

79. The dyeing of wool-cotton unions to solid shades is usually accomplished from a single bath at neutral or slightly alkaline pH. Dyeing of the vegetable fibers is effected by the use of direct dyes whose color salts contain such chemical

groups as disazo, trisazo, tetrakisazo, stilbene, and thiazol. Direct dyes exhibit varying dyeing affinities and fastness properties. A number of the direct dyes will dye wool and cotton nearly the same shade from a single bath. Although these dyes may seem to be ideal for wool-cotton unions, they are often unsatisfactory because they possess poor fastness properties to light, perspiration, and wet treatments. Satisfactory fastness of direct dyes for wool-cotton unions is obtained with direct dyes having a minimum affinity for wool. All of the direct cotton dyes, however, stain wool if applied at the boil.

Like wool dyes, direct cotton dyes are characterized by their varying degrees of levelness. Highly dispersed direct dyes, designated Class A, exhibit excellent level-dyeing properties. They show an increasing affinity for cotton at temperatures of 120 F to 200 F. At a temperature of 212 F, however, they produce dyeings of somewhat lower color value. This phenomenon is explained by the truly molecularly-dispersed condition of Class A dyes at boiling temperatures that causes increased mobility between the cellulose fibers and dye liquor. Class C direct dyes are highly aggregated and are of poor level-dyeing properties. Class B dyes possess intermediate level-dyeing ratings. Table 9 shows a few typical direct cotton dyes that are employed for wool-cotton union dyeing.

80. The use of dyeing assistants for the application of direct dyes is largely confined to sodium chloride. This also satisfies the needs of most neutral-dyeing acid dyes. The function of the sodium chloride, or common salt, is that of contributing to dye aggregation, because of its electrolytic nature. In wool-cotton union dyeing 2% to 10% common salt produces satisfactory results for most shades. Excessive amounts of common salt should be avoided, since precipitation

TABLE 9

DIRECT COTTON DYES

Dyestuff	C. I. Name
CLASS A	
	DIRECT
Chrysophenine Conc.	Yellow 12
Calcodur Red 8BL	Red 81
Amanil Brilliant Violet 4B	Violet 29
CLASS B	
	DIRECT
Pontamine Violet N	Violet 1
Diphenyl Fast Orange WS	Orange 29
Erie Bordeaux B	Red 13
Amanil Navy Blue SWC Ex.	Blue 24
CLASS C	
	DIRECT
Chloramine Black BH	Blue 2
Erie Fast Brown B Conc.	Brown 31
Chlorantine Fast Brown BRLL	Brown 95
Amanil Green B Conc.	Green 6

of the dyestuff will result, causing bronziness of shade due to a dye deposit of increased particle size.

The liquor ratio is also of primary importance in union dyeing. It should be maintained in amounts of 1 part of material to 10 to 15 parts of water, in order to effect proper exhaustion. If larger proportions of liquor are used, greater amounts of common salt will be required to promote complete exhaustion of the dye bath.

Color Application to Wool-Cotton Blends

81. The bath is prepared with 2% to 10% common salt followed by the addition of the dyestuff, previously dissolved in hot water. For darker shades, larger amounts of common salt, 10% to 20%, may be required to obtain exhaustion. One half of the salt is added at the start of the dyeing, and the remaining half after the dyeing is in progress, to promote uniform exhaustion.

If slower exhaustion of the dye bath is desired, the common salt is replaced by an equivalent amount of Glauber's salt. The temperature of the bath is raised to the boil in 45 min and boiling continued for 15 min, after which time the steam is shut off and the bath allowed to cool to between 120 F and 180 F. Color development for the wool fibers is attained at temperatures of 180 F to 212 F, and for the vegetable fibers at temperatures of 120 F to 180 F. A major concern in union dyeing is the manipulation of the temperature control, to obtain a desired balance of shade between the mixed fibers. In wool-cotton union dyeing, solid appearances of shade are imparted by maintaining the wool fibers lighter in shade and the cotton fibers slightly darker

Aftertreatments

82. Most direct dyes are deficient in fastness to water, light, and alkalis. Improved qualities of fastness are obtained for wool-cotton union materials by means of aftertreatments. Direct dyes, whose molecular structure contains, as end components, two hydroxyl or two amino groups in the meta position, can be made more resistant to water by aftertreating with 2% to 4% formaldehyde at 140 F for 30 min. Because shade changes may result from this treatment, it is used only on dark shades and blacks. Minimum changes of shade are obtained for all colors by the use of fixing salts CMS, an auxiliary product which is a buffered mixture of aluminum and chromium salts. Their application is made in amounts of 2%, with 10% common salt, at 70 F for 10 min, followed by rinsing.

83. Improved light fastness for some direct dyes is gained by aftertreating with 1% to 3% copper sulfate, and 2% to 5% acetic acid, at a temperature of 140 F to 180 F for 30 min. Shade changes of direct dyes with copper salts vary, but the majority of direct dyes do change shade. Direct dyes of the Class C type are marketed for copper treatment under such names as *Benzo Form, Solophenyl, Pyrazol, Cuprofix, Resofix,* and *Coprantine.* Improved fastness to washing for most of these dyes is obtained by the addition of urea formaldehyde or melamine

resin to the copper bath. Wash fastness up to 160 F is obtained for some of the direct cotton dyes.

Enhanced fastness to alkalis and washing is attained for certain direct dyes by diazotizing and developing. Direct dyes adaptable for such a treatment contain diazotizable groups, NH_2. Such dyes show a deepening of their shade during development. After direct dyeing of the wool-cotton union material, diazotizing of the direct cotton dyes is accomplished by aftertreating for 20 min in a cold fresh bath of $1\frac{1}{2}\%$ sodium nitrite and 3% sulfuric acid, following by washing. Color development is obtained with the addition of $1\frac{1}{2}\%$ beta naphthol, or m-tolylenediamine, in the presence of 1% caustic soda, or 3% sodium carbonate, cold for 20 min, followed by washing. The alkali provides solubility of the developers. Dark shades of union material employed for such purposes as ski cloth or shoe tops may be diazotized and developed.

Wool-Rayon Blends

84. Union fabrics of wool and rayon are dyed in the same way as wool-cotton unions, since rayon has an affinity for direct dyes. As with all types of materials prepared for dyeing, the complete removal of oil, size, and alkalis is necessary for satisfactory dyeing results. Insufficient removal of oil and sizing material results in poor penetration of the dye in the fibers.

Incomplete removal of residual alkali promotes the reduction of certain direct dyes in the presence of rayon, with the result that they produce a false shade. For example, Diamine Fast Blue FFB, C.I. Direct Blue 71, may dye to a red-orange, instead of to its blue color. Cotton, however, having only weak reducing properties, does not cause similar changes of shade. To insure against the incomplete removal of residual alkali from wool-rayon materials, the addition of 1% ammonium sulfate is recommended. This will minimize, or prevent completely, objectionable changes of shade.

Wool-Cotton-Rayon Blends

85. The same methods of color application are employed for a three-fiber blend of wool and cellulose as for the two-fiber blends already discussed. The dyeing problem, however, is more complicated, since most direct dyes do not possess equal affinities for both cotton and rayon.

Direct cotton dyes, Class C, which display a rapid rate of exhaustion, have a tendency to dye the rayon darker than the cotton. As a result of this fiber selectivity of direct dyes, union dyeings are produced which reveal a pronounced difference in shade between the two cellulosic fibers. Dissimilar affinities of direct dyes for cotton and rayon fibers are overcome by the use of direct dyes which exhibit similar level-dyeing rates and the same degree of exhaustion. Further assistance in promoting uniformity of shade between cotton and rayon fibers is afforded by the introduction of sodium stannate to the dye bath. Sodium stannate

is absorbed to a greater extent by rayon than it is by vegetable cellulose fibers; thus the affinity of the direct dyes for rayon is somewhat retarded.

Vat Dyeing of Blends

86. Improved fastness properties for wool-cellulose unions are obtained with vat dyes. These are applied with conventional cotton dyeing machinery, such as jig or continuous dyeing processes. Wool fiber degradation in blends of 80% rayon and 20% wool, if kept to a minimum, does not affect to any great extent the wearing qualities of such fabrics, their resistance to abrasion, or their hand. Better dyeing results, in qualities of penetration and solidity of shade, are attained by vat dyeing, especially for certain fabric constructions, than are possible by kettle dyeing. However, to avoid excessive fiber damage to the wool, it is necessary to employ discretion in selecting vat dyes. There must be strict control of temperature and alkali concentration.

The application of vat dyes for light shades is made by padding the reduced vat dye. This is followed by re-reduction in a continuous process, utilizing either the Williams machine or the Du Pont process. Medium and dark shades are dyed by padding the unreduced vat dye, or pigment, followed by reduction in the jig or continuous process. Blends which contain wool in excess of 20% are best dyed by the use of a milder alkali, such as trisodium phosphate, and selected vat dyes, with which complete reduction is effected. Protective colloids such as glue and sodium lignin sulfonate are also employed to assist in the prevention of wool fiber degradation.

Wool-Acetate Blends

87. The dyeing of acetate demands the use of a special group of highly molecularly-dispersed dyes. These are of two general chemical types, namely, the insoluble azo and the aminoanthraquinone. To assist in the dispersion of acetate dyes, sulfonated fatty alcohols are usually added to the dye bath. Acetate dyes have pronounced affinities for wool fibers, but as a class they exhibit poor-to-moderate fastness properties on wool. The resistance to light, washing, and gas fading is poor.

Good fastness properties of wool-acetate unions are obtained with blends that contain only 10% to 20% of acetate. Neutral dyeing, Group C, acid dyes are employed for the wool. Acetate is used to advantage as a decoration yarn for wool-cotton-viscose blends, because acetate has no affinity for the majority of acid and direct dyes. The dyeing of black with acetate is accomplished by diazo-tizing dianisidine and developing with beta-hydroxynaphthoic acid. Temperatures of no higher than 185 F are maintained in dyeing acetate, in order to preserve the luster of acetate yarns.

Wool-Nylon Blends

88. The wearing qualities of wool fabrics are considerably lengthened when

nylon staple is added to the spinning mixture. This is due to the fact that nylon has great tensile strength. Nylon is a synthetic polymer whose chemical structure is composed of polypeptide chains. Having a chemical character like that of wool and silk, nylon possesses protein-like properties such as an affinity for wool dyes.

Nylon is a thermoplastic material having elastic properties. It stretches considerably under tension and at elevated temperatures, a fact that contributes to the formation of wrinkles or to the lashing of wool-nylon piece goods during dyeing. Before dyeing it is absolutely necessary to "set" nylon or nylon-containing fabrics at temperatures greater than will be encountered during dyeing or subsequent operations. Setting is accomplished by the use of steam under pressure, or with dry heat, at temperatures of about 400 F.

Nylon is chemically unaffected by the use of organic acids in amounts employed for the application of acid dyes. With mineral acids, however, a pronounced reduction in tensile strength results, followed by a further degradation on aging.

89. For the dyeing of wool-nylon blends, neutral-dyeing acid dyes, Group C, are best suited. Although they fulfill most of the requirements, they are not completely satisfactory. The majority of wool dyes dye nylon and wool different depths of shade from the same bath. This marked individuality of nylon with respect to acid dyes is annoying, since it causes nylon to absorb only certain colors from a given dye bath, producing two-tone and unsolid effects on wool-nylon unions. Consequently, a correct balance of the dyestuffs used is of the utmost concern in producing solid shade effects.

Acid dyes for nylon, particularly Groups A and B, have a low point of saturation, thereby presenting a difficult task for the uniform dyeing of dark shades of wool-nylon blends. Chrome dyes, on the other hand, do not form the chrome dye complex on nylon as readily as they do on wool. However the chrome dye complex can be satisfactorily formed on nylon yarn by application of the top-chrome method, followed by a steaming treatment at a pressure of 8 lb at 235 F. Dyes which show a pronounced change of shade with bichromate are unsuitable for use in wool-nylon piece dyeing. Metalized dyes are unsatisfactory for wool-nylon blends because the sulfuric acid necessary for their application promotes a reduction in the tensile strength of the nylon fibers.

Acetate dyes possess excellent dyeing properties when added to nylon producing extremely level dyeing results. Their use for wool-nylon blends, however, is not satisfactory, because of their inferior fastness properties to wet treatments and light. Direct dyes have no marked affinity for nylon from a neutral bath, but from an acetic acid bath they develop increased affinities. Nevertheless, their use is still unsatisfactory owing to their inferior fastness properties on nylon. Vat dyes, as a class, produce poor fastness to crocking, washing, and light when applied to nylon.

90. For wool-nylon blends, the same method of dye application is employed as for all-wool material, with the use of Group C neutral-dyeing acid dyes. Dyestuff selectivity is, of course, the keynote in the successful dyeing of wool-nylon blends. The suitability of individual dyestuff in the Group C acid dyes is determined by trial-and-error laboratory dyeings. For example, Alizarine Cyanine Green, C.I. Acid Green 25, and Anthraquinone Violet, C.I. Acid Violet 34, dye the wool and nylon approximately the same shade from a single bath; whereas Alizarine Supra Blue A, C.I. Acid Blue 25, and Alizarine Sky Blue B, C.I. Acid Blue 78, dye the nylon heavier than the wool in light-to-medium shades. Dark navy shades, even with Group C acid dyes, are difficult to obtain because of their lower saturation value on nylon, which results in two-tone effects. The light fastness of neutral acid dyes on wool-nylon unions is slightly inferior to that on all-wool materials. Fastness to wet treatments is satisfactory.

Dyeing Machinery

Types of Dyeing Machinery

91. The particular type of dyeing machinery to be employed for wool dyeing depends upon the form in which the raw material is to be dyed. Subsequent manufacturing operations and the ultimate use of the material must also be considered. Raw wool is dyed, after scouring, in the form of clean stock. Wool may also be dyed in the form of worsted tops or slubbing, yarn skeins, packaged yarn, felt, and woven or knitted piece goods.

Raw Stock Dyeing

92. With the raw stock dyeing machines, the principle of operation is the circulation of the dye liquor through the mass of wool fibers. An example is the Riggs & Lombard stainless steel stock-dyeing machine, shown in section in Fig. 4. In the cylindrical tank *1* is placed the wool stock *2*. This tank is equipped with a perforated false bottom *3* and up through the center of the tank extends a perforated pipe *4*. An expansion tank *5* serves as the heating chamber, and is also used for dye additions. A motor *6* furnishes the power to drive the propeller *7*, which moves the dye liquor in the direction shown by the arrows. The dye enters a duct *8* at the bottom of the dye kettle, the duct being connected to the perforated pipe, and forces its way evenly through the wool stock. Constant circulation is attained by overflow of the dye liquor *9* into the expansion tank.

During the dyeing period a perforated plate *10* is placed on top of the wool stock, to keep it in place and prevent plugging of the exit duct *11*. The whole unit is let into the floor *12*. A steampipe *13* serves to heat the dye liquor. A drain *14* is used to remove the surplus liquor after dyeing. The wool stock, weighing about 500 lb, is raised from the dye kettle by an electric hoist.
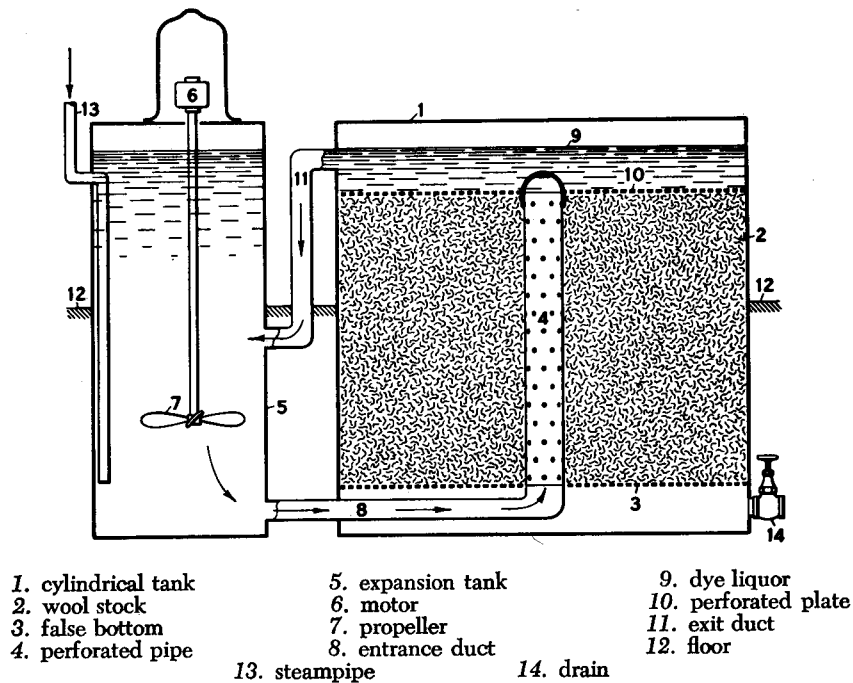
1. cylindrical tank   5. expansion tank   9. dye liquor
2. wool stock   6. motor   10. perforated plate
3. false bottom   7. propeller   11. exit duct
4. perforated pipe   8. entrance duct   12. floor
                    13. steampipe   14. drain

FIG. 4. STOCK-DYEING MACHINE

93. Of importance in the operation of the raw-stock dyeing machines is the uniform packing of the wool stock, to avoid channeling of the dye liquor, which is a cause of uneven dyeing. Also important is the use of acid and chrome dyes that dissolve readily in small volumes of water; otherwise precipitation and localized dyeing may result. The use of stainless steel equipment for wool dyeing aids materially in the production of bright pastel shades. It also reduces cleaning to a minimum in the dyeing of dark shades, when this is to be followed by the dyeing of light shades.

Top, or Slub, Dyeing

94. Worsted tops, or slubbing, are dyed by the following three systems: 1) pot, 2) spindle, and 3) Abbott. The pot system uses individually enclosed stainless-steel pots built into the dye kier of the machine. The pot system is employed for the dyeing of extremely fine grades of worsted fibers in small lots, each pot accommodating a worsted top weighing about 20 lb.

Spindle System

95. The spindle system uses the spindle type of top-dyeing machine, shown in section in Fig. 5. This type of machine provides for increased production. The dye kettle 1 is rectangular. It may be constructed of wood lined with stainless steel, or it may be wholly of stainless steel. The worsted tops 2 weighing about 12 lb. each, are placed over perforated stainless-steel spindles 3 that extend through the center
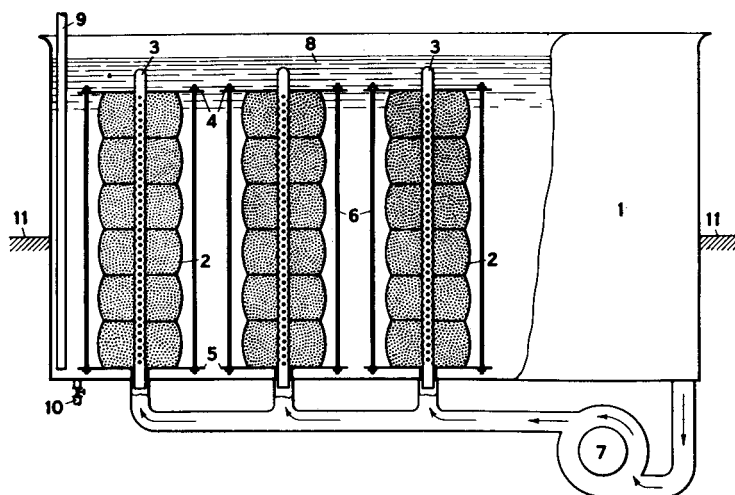
1. dye kettle
2. worsted tops
3. perforated spindles

4. top plate
5. bottom plate
6. rods

7. pump
8. dye liquor
9. steampipe

10. drain   11. floor

FIG. 5. SPINDLE TYPE OF DYEING MACHINE

holes of the tops. The diameter of each spindle is $2\frac{1}{4}$ in. The tops are compressed and held in place by top plates 4 and bottom plates 5, and secured in position by rods 6. The dye liquor is circulated by means of a pump 7 up through the perforated spindles. Although the flow of dye liquor in the machine illustrated is in one direction only, spindle dyeing machines with a reversible flow are available. The dye liquor 8 is heated by a steampipe 9. Surplus dye liquor flows out through a drain 10. The whole machine is built into the floor 11. Top-dyeing machines are designed with 2 to 10 spindles. The spindles vary in length and are capable of holding anywhere from 3 to 13 worsted tops each.

Another type of spindle dyeing machine is the Steinen-Obermaier, which is of circular construction. Pressure on the tops is attained through a compression plate by turning down the handle of the plate. The Steinen-Obermaier machine also employs a separate heating and dyestuff-feeding tank.

With the spindle type of dyeing machine, the flow of dye liquor is maintained at a low pressure. Fiber disturbance and felting are kept to a minimum by wrapping each top separately in cotton cheesecloth before placing it on the spindle. After dyeing, the tops are vacuum-extracted, removed from the spindles, and backwashed. During the backwashing process the tops are midly scoured and loose dyestuff is removed. Backwashing is followed by drying and gilling. Additional blending and straightening of the dyed fibers is obtained with two or three extra gillings, a procedure which is often necessary with unevenly dyed tops.
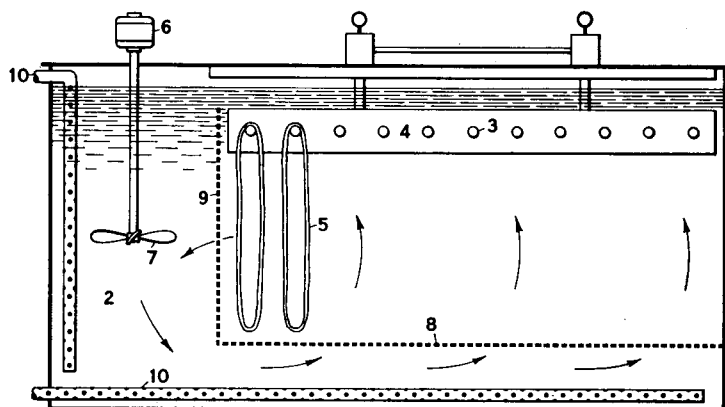
1. dyeing section
2. propeller chamber
3. steel rods
4. skein frame
5. yarn skeins

6. motor
7. propeller
8. perforated false bottom
9. perforated partition plate
10. steampipes

FIG. 6. HUSSONG SKEIN-DYEING MACHINE

Abbott System

96. The Abbott system differs from the spindle system in that the wool slubbing is wound uniformly onto perforated stainless-steel jack spools. Abbott dye kettles are available with 2-, 6-, or 18-spool capacity. Of circular design, they are of wood lined with aluminum or are entirely of stainless steel. The jack spools, which have a 6-in. diameter for the dye liquor passage, allow for the winding of 2 to 2½ in. of slubbing weighing approximately 25 lb.

In the spindle system the dye liquor must travel through 6 to 8 in. of wool stock. In the Abbott dye kettles, the distance that the dye liquor must travel is reduced to 2 or 2½ in. of wool stock. Dyeings by the Abbott system, therefore, are of excellent character, producing uniform results from the center to the outside of the wound slubbing. In volume of production, however, the Abbott system lags behind the spindle system; it also requires the use of special winders to transfer the slubbing from the ball top to the jack spools. Drying is accomplished with hot-air dryers capable of accommodating 18 spools. Backwashing is not necessary when the Abbott system is used.

Yarn Dyeing

97. The dyeing of yarn is performed by two basic systems: 1) the skein system and 2) the package system. Skein dyeing has long been in use. At first it was performed by hand, the skeins being suspended from sticks into rectangular vats. The position of the skeins was periodically changed by rotation, to prevent marking and unlevel dyeings.

With the introduction of the Klauder-Weldon machines, machine skein dyeing

began. In these machines, the skeins are rotated in the dye liquor by mechanical means. The machine employs two pairs of wheels, one pair on each side of a semicircular vat. Each pair of wheels consists of a smaller wheel within a larger wheel. The skeins are suspended between wooden rods attached to the wheels. At each revolution of the wheels the wooden rods make a quarter turn, causing the skeins to change their suspended position and preventing stick marks. Although the Klauder-Weldon is still employed for the dyeing of fine woolen yarns, it has lost considerable ground owing to its low production.

Skein Dyeing

98. Most modern skein-dyeing machines employ means of circulating the dye liquor, the skeins remaining stationary during dyeing. This principle of operation is used in the Hussong, the Steinen-Obermaier, and the Smith, Drum, and Company machines. The Hussong machine, diagramed in Fig. 6, is of rectangular design and is constructed of stainless steel. It consists of two sections: the dyeing section *1* and the propeller chamber *2*. Stainless-steel rods *3* are fitted into the skein frame *4*. The skeins *5* are suspended from these rods. A motor *6* drives the propeller *7*, which forces the dye liquor downward. The liquor then moves up through the perforated false bottom *8*, through the wool skeins, and through the perforated partition plate *9*. The Hussong dyer is equipped with a two-pipe steam-heating arrangement *10*. The pipe that runs the entire length of the kettle is employed to raise the temperature of the dye bath near the boil. This pipe is then shut off to avoid tangling of the skeins by the ejected steam. A temperature near the boil is maintained by having steam enter only through the pipe in the propeller chamber.

The Steinen-Obermaier machine, which is similar to the Hussong, also employs two sections. In this machine the larger section serves as the dye kier and receives the yarn carrier. The smaller section serves as the dyestuff-feeding tank and the heating unit. The skeins are held in position at the top and bottom with sticks, thus preventing swirling of the skeins during dye circulation. Single Steinen-Obermaier skein-dyeing machines have a capacity of 250 lb; additional units can be coupled for increased production. One or several units can be used to obtain a single shade.

Package System

99. The principal of package dyeing is very similar to that of the Abbott system for dyeing slubbing. In fact, yarn may be wound on jack spools and dyed on the Abbott system, just like slubbing.

All package-yarn dyeing machines use a circulating method for the dye liquor. The Smith-Drum dyeing machine has a circular kettle. The yarn is wound on perforated tubes or muslin-covered springs and placed on the spindles of the material carrier. The center manifold of the carrier is the passage for the dye
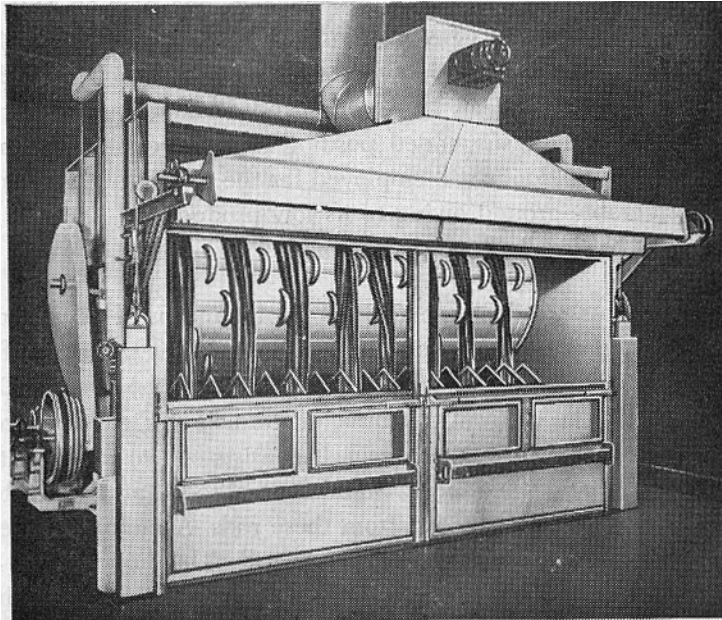
FIG. 7. PIECE DYE KETTLE

liquor. The dye liquor is pumped equally in both directions of the carrier, through the packaged yarn. An expansion tank provides for dyestuff additions, and serves as a heating unit and as an overflow for constant circulation. Dye circulation for reverse flow is automatically controlled.

Felt Dyeing

100. Rotary dyeing machines are commonly used for the coloring of felt hats made from wool or fur. The hat bodies are first packed into the compartments of the rotating cylinders of the dyeing machine. The cylinders are then partly submerged in the dye liquor. Dyeing is affected by the hat bodies being alternately raised and dipped into the dye liquor as a result of the circulating motion of the cylinders. Other machines, such as the Steinen-Obermaier, use a propelled circulating system for the dye liquor. In these machines the hat bodies rest on a perforated false-bottom plate. They are periodically tumbled to the opposite side of the dye tank by means of a center plate, at which time the flow of the dye liquor is reversed.

Piece Dyeing

101. In raw stock or yarn dyeing the material is held stationary while the dye liquor is in motion. In piece-dyeing machines, such as the one shown in Fig. 7, the dye liquor remains in the bottom part of the machine. The piece goods are

(a) Front view (b) Side view

1. piece goods
2. dye liquor
3. revolving drum
4. perforated plate

5. steam inlet
6. water inlet
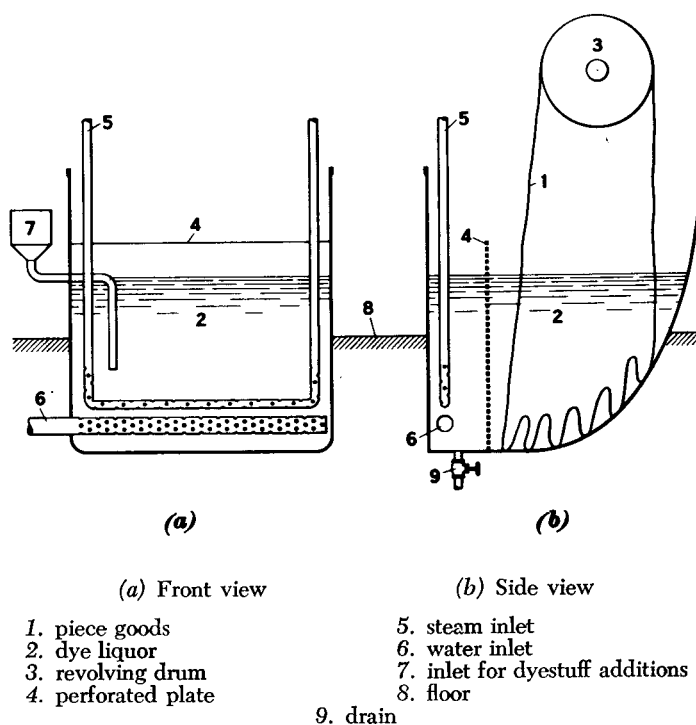7. inlet for dyestuff additions
8. floor
9. drain

Fig. 8. Piece Dyer Sections

moved through the dye liquor somewhat in the same manner as in a piece-goods washing machine.

To make the operation clear, the machine is shown in two sections in Fig. 8. Piece gods are woven in cuts measuring approximately 70 yd in length. These are sewn end to end to form a continuous rope. The piece goods *1* are set in motion through the dye liquor *2* by a revolving drum *3*. A perforated plate *4* separates the material from direct contact with the inlets for steam *5*, water *6*, and dyestuff additions *7*. Like most other dyeing machines, the piece dye kettle is let into the floor *8* and a drain *9* is provided for the disposal of surplus dye liquor.

102. In some dyeing machinery, particularly in machines for piece kettle dyeing, the distribution of heat between the front and back ends of the kettle is not uniform because steam enters only at the front. Variations in temperature of 10 F to 20 F may exist from front to back. Temperatures at near boil should therefore be maintained in dyeing, to produce satisfactory results. Care should also be exercised to maintain a proper water-to-cloth ratio. Additions of dyestuff should be made cautiously when such additions are necessary to match a given shade, because dye streaks occur readily. The Riggs and Lombard piece dye kettle is equipped with multigrip humps on its revolving drum. These humps

serve to change the position of the folds. This feature is especially necessary for heavy-weight fabrics, since it eliminates one of the causes of uneven or streaky dyeing. Another help in overcoming folds caused by the rolling of piece goods is found in tacking, or sewing together, the selvages of the cloth, with the face of the fabric inside. Tacking causes the fabric to balloon, thereby changing the position of the folds.

Special Dyeing Conditions

Shade Variations in Wool Dyeing

103. Shade variations in wool dyeing do not occur only because of mechanical deficiencies of the dyeing machinery, but also because of differences between wool lots. The reasons for such variations of shade are numerous, and often they are related to the condition of the wool fibers or to the treatments given them previous to dyeing. There may be differences in particular grades of the wool stock, conditions resulting from the effect of climate on the wool, insufficient or uneven removal of oil and soap in scouring, acid- or alkaline-damaged wool fibers, and variations of pH.

Such treatments as bleaching and chlorination also impart shade variations. Wool chlorination is employed in the production of nonshrinkable woolens, being attained by either the acid or the alkaline process. The acid process promotes increased affinity of the wool for dyestuffs, whereas the alkaline process, like bleaching, retards the affinity of the wool for wool dyes.

Water Supply

104. The availability of soft water in a dyeing and finishing plant is of paramount importance if satisfactory dyeing results are to be achieved. In some localities water contains large amounts of calcium and magnesium metals in the form of sulfates, causing the water to be hard. Subsequently, as a result of the scouring operation, these metal sulfates form insoluble complex calcium and magnesium soaps, and as such have greater affinity for wool. Their presence on the wool fibers interferes with the uniform diffusion of the dye ions, and the resultant dyeings have a skittery, or unsolid and streaky, appearance.

The addition of sodium carbonate to hard water helps to make the calcium and magnesium sulfates harmless by converting them to soluble carbonates. Many plants that have hard-water problems use water-softening systems, the zeolite process being the most common. This process removes the calcium and replaces it with sodium.

Pulled Wools

105. Another cause for the presence of calcium in wool fibers is the use of lime to assist in the removal of wool fibers from the hides when producing pulled wool. Although the percentage of wool obtained as pulled wool is small, the

presence of calcium will cause serious dyeing difficulties. Polyphosphates, such as *Calgon*, a molecular dehydrated sodium hexametaphosphate $(Na_2PO_3)_6$, *Quadrafos*, $Na_4P_6O_{18}$, the sodium tetraphosphate, $Na_6P_4O_{13}$, and the organic sodium salt of ethylenediamine tetraacetic acid, are used to remove the calcium. These polyphosphates are also valuable in helping to remove insoluble aluminum soaps in the presence of an alkaline medium such as ammonia.

Other metals that may cause difficulties in dyeing, such as shade changes and stains, are iron and copper. For that reason it is best not to use brass and copper piping. The solubility of iron from pipes, tanks, and other fixtures can be held at a minimum by keeping the water supply at neutral or slightly alkaline pH.

Controlling the Dyeing Process

106. Very often faulty dyeings arise from improper control of the dyeing process. Correction of such dyeings is necessary to render them commercially acceptable. When off-shade goods are heavier in shade than is desired, it is necessary to remove some of the dye from the wool fibers, and then to replace the required amount of color to obtain a satisfactory match.

Defects of color in wool materials dyed with groups A and B acid dyes are easily rectified if the cause is improper color application. When there is need for the removal of only a small amount of color, neutral or slightly alkaline salts are used. Glauber's salt, in amounts of 10% to 40% applied from a boiling bath, works very well. To remove excessive amounts of color, or for the correction of faulty dyeings, 2% to 5% ammonia is used together with 10% to 20% Glauber's salt. The temperature of the bath is raised in $\frac{1}{2}$ hr to 180 F to 200 F. Part of the removed dyestuff is then replaced on the material, with the addition of sulfuric acid. Neutral or chrome dyes, however, which possess greater fastness to alkaline treatments, are not effectively corrected by such a procedure.

Stripping

107. Wool-dyed materials that cannot be corrected by the ammonia treatment require the use of stripping agents. These agents cause the destruction of the dyestuff through oxidation or reduction. The reduction method of stripping is generally used. It is accomplished by the use of either sodium sulfoxylate formaldehyde or the zinc salts of the sulfoxylate formaldehyde. The sulfoxylates, however, are only soluble from an acid bath, from which they exert powerful reducing properties. The zinc salt is more commonly used for stripping because of its lower cost. A low *p*H with sulfoxylates must be avoided; otherwise rapid decomposition results, with poor penetration and uneven color destruction.

Organic acids, such as acetic and formic, are very good for stripping. Their lower acidity provides gradual reduction and uniform color decomposition. Carbonized materials containing sulfuric acid should be neutralized before stripping. The stripping process, however, will always cause some damage to the

wool fibers. For that reason it should be employed with discretion. Whenever possible, redyeing into a darker shade should be given preference, and stripping only resorted to when everything else fails.

108. Azo dyes are easily destroyed by the sulfoxylates, but wool dyes of the triphenylmethane, anthraquinone, and azine class strip with difficulty. Wool Fast Blue, C.I. Acid Blue 59, for example, is reduced to its leuco compound, a tan color, but on oxidation with washing it reverts to its original blue color.

For best results in stripping, the temperature of the bath is maintained just below the boil. The bath contains 2% to 4% zinc sulfoxylate formaldehyde in the form of Parolite, Formopon, or equivalent brands, and 1% to 3% formic acid or 2% to 5% acetic acid of 56% strength. The temperature of the bath is raised in $\frac{1}{2}$ hr to 205 F to 210 F, and maintained at that point for 20 to 30 min. A thorough wash after stripping is necessary to avoid contamination of the dye bath with sulfoxylate, which will cause dyeing difficulties. With the application of chrome dyes, the stripped material must be neutralized with 1% to 3% ammonia at 120 F to 180 F for 20 min, followed by washing.

Sodium hydrosulfite, $Na_2S_2O_4$, is also employed as a stripping agent. It exerts reducing properties equally as strong as those of the sulfoxylates, but in the presence of wool its action is lessened because of its instability. It decomposes rapidly at low temperatures, and therefore produces unlevel and insufficient color destruction. Sodium hydrosulfite nevertheless finds use in the removal of small amounts of wool dye. Of more importance is its use in the destruction of direct cotton dyes on wool-cellulose materials. It is also used to clean stained effect threads of cotton and rayon employed as decoration yarns on wool fabrics.

Stripping with hydrosulfite is done in amounts of 2% to 6%, made alkaline with 1% to 3% sodium carbonate or 2% to 5% ammonia. Stripping is carried out at 120 F to 180 F for 20 to 30 min, followed by thorough washing.

Textile Dyeing

PART 2

Examination Questions

Notice to Students.—Study this instruction text thoroughly before you attempt to answer the following questions. Read each question carefully and be sure you understand it; then write the best answer you can. The first five questions require you to choose one of several 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. When your answers are completed, examine them closely, correct all the errors you can find, and see that every question is answered; then mail your work to us.

1. Some acetic acid dyes are difficult to exhaust. To promote better exhaustion: (3%)

    a) a small percentage of sulfuric acid may be added to the dye bath.

    b) sodium carbonate may be employed instead of Glauber's salt.

    c) the material may be pretreated with ammonia.

    d) a little phosphoric acid may be used in the solution.

2. A men's wear suiting material has been dyed with indigo. Complaints are received that the color is rubbing off. The cloth should have been: (3%)

    a) dyed with a chrome dye instead.

    b) scoured and rinsed after dyeing.

    c) treated with sodium carbonate.

    d) stripped with a solution of sodium hydrosulfite.

3. Acid dyes are satisfactory for many purposes. They should not, however, be used for: (3%)

    a) women's suitings.   *c*) men's sport shirtings.

    b) children's coatings.   *d*) knitting yarns.

4. The bottom-chrome method is preferred for dyeing densely woven worsted fabrics because: (3%)

    a) of its higher color value.

    b) it has excellent penetrating qualities.

    c) this method is shorter, and therefore cheaper.

    d) damage to the wool is prevented.

5. A dye bath prepared with a level-dyeing acid dye can be exhausted with the assistance of sulfuric acid. However, the resulting dyeing is apt to look streaky. To get better results: (3%)

    a) hydrochloric acid should be used instead of sulfuric acid.

    b) Glauber's salt should be added to the dye solution.

    c) acetic acid should be mixed with the dye before it is dissolved.

    d) the material should be soaked in a borax solution prior to dyeing.

6. Why are small variations of color not too important in stock or top dyeing?
(6%)

7. Explain briefly why Group C acid dyes should not be used when it is necessary to add a little dyestuff during dyeing, in order to match a given shade.
(8%)

8. What will happen if the wool in a raw stock dyeing machine is packed in uneven lumps?
(8%)

9. When are zinc salts employed in connection wth wool dyeing? (8%)

10. Why is a temperature of 212 F considered as the standard temperature for wool dyeing?
(6%)

11. A dye bath is to be prepared to dye 1,000 yds. of flannel for women's wear to a deep wine red. The cloth weighs 8 oz. per yd. How many pounds of sulfuric acid and how many pounds of Glauber's salt will be needed?
(12%)

12. What makes diammonium phosphate an ideal assistant for the application of colloidal dyes?
(6%)

13. A steampipe runs the length of a skein-dyeing machine and is used to heat the dye bath before the skeins are inserted. Briefly explain why this pipe must be shut off, and how the dye bath is kept hot, during dyeing. (8%)

14. Carbonized woolen goods are to be dyed dark red with acid metalized dyes. Tests reveal that the goods contain 3% acid. What preparation does the dye bath need?
(8%)

15. You are to dye a 500-lb lot of woolen piece goods with Supralan Red B. Color additions, if required, will be made at the boil. List the types and amounts of dyeing assistants and the dyeing procedure you would use. The amounts are to be based on the weight of the goods. (15%)

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