Chapter 7

IDENTIFICATION OF DYE CLASSES ON FIBERS

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There are many obvious reasons why the identification of the class of dye used in a dyeing or print is important, e.g., fastness problems, choice of finishing treatments or analysis of complaints. This identification is facilitated by knowledge of the identity of the fiber which is a substrate for the dye, since procedures are based on selectivity of classes of dyes for fibers according to chemical composition. Fiber identification suggestions are included in this text; a detailed procedure is de-

scribed in AATCC Test Method 20-1977 (*1*). Positive identification of a particular dye present on a fiber is, in most cases, extremely difficult, if not impossible with our present choice of methods or equipment, and all practical systems of identification are based on dye classes rather than on specific members of the class.

A comprehensive and sophisticated methodology for the identification of individual dyes can be found in Venkataraman's text (*2*).

One of the earliest of such systems was that of Green (*3*), which although now out of date, is still a useful reference. Clayton (*4*) published an up-dated version in 1946 and a second edition in 1963. A very good discussion of methods for identification of dyes on the fiber is given in Volume 4 of Garner's manual (*5*). Derrett-Smith and Gray (*6*) have recently published an excellent discussion of the identification of vat dyes on cellulosic materials. This chapter offers a system of identification based on work by the New York Section of the AATCC (*7*) and was published as a preliminary report (*8*) and as a chapter in the Second Edition of *Analytical Methods for a Textile Laboratory*, published under the aegis of AATCC committee RA72.

The schemes of analysis presented here include tests for the identification of the fiber and are based on both a systematic exclusion of dyes which might be present, and a focusing of attention on a limited number of remaining possibilities.

Whenever possible, the suggested procedures employ laboratory tests and techniques available in practically all textile laboratories. More elaborate methods of analysis which may possibly be useful in dye identification are discussed in other chapters of this book. There is no doubt that these methods will find increasing use in the future.

The identification of dyes in blends of fibers is not yet clearly established, but the more experienced analyst will be able to adapt these procedures to such problems.

Dyes On Cellulosic Fibers

Cellulose fibers are rapidly recognized by even burning, soft ash, no bead and an odor characteristic of burning paper.

After the fiber has been identified as cellulosic, then a systematic separation of the dye is necessary to determine which of the following possible classes has been used: direct, acid, basic, direct-aftertreated with resins, sulfur, vat, oxidation blacks (aniline and diphenyl) direct-aftertreated with metals, direct-aftertreated with formaldehyde, naphthols and insoluble azo, diazotized and developed, pigments, and fiber reactive. Identification of dye classes on either cotton or rayon follows the same procedure. Solution-dyed viscose is usually identified by microscopic examination of a fiber cross section.

Group I

Group I includes direct, acid, basic and direct dyes aftertreated with resins.

These dyes are not set apart as a group by any single test, but are classified by their bleeding in dilute ammonia or acetic acid provided the extractions are carried out in the prescribed order.

DIRECT DYES. A 100-300 mg portion of the dyed sample is placed in a 35 ml test tube, 5 to 10 ml of water and 0.5 to 1 ml of concentrated ammonia are added and the mixture boiled in order to bleed off a sufficient amount of dye for redyeing a piece of white cotton cloth.

When a sufficient amount of dye has bled from the sample, the sample is removed, a piece of white cotton cloth weighing 10-30 mg is placed in the test tube and 5 to 30 mg of common salt added. After boiling gently for 40-80 sec and cooling to room temperature, the cotton is removed, rinsed and examined.

Redyeing on cotton in an ammoniacal solution in the presence of salt to a shade and strength comparable to the shade and strength of the original sample is definite evidence of a direct dye.

ACID DYES. Acid dyes are used very little on cellulosic fibers except for identification or for the dyeing of acid dyeable rayon.

If the sample in the test for direct dyes bled but left the test cotton white or only slightly stained, the colored extract is neutralized with acetic acid, 1 ml of 10% acetic acid is added, and 10-30 mg of white wool is placed in the liquor. After boiling for approximately half a minute, the wool is rinsed and examined.

Redyeing on wool from an acid bath indicates the presence of acid dyes, provided the presence of a direct or basic dye is not shown.

BASIC DYES. Basic dyes have been used very little on cellulosic fibers in recent years since the advent of fiber reactive colors. They may be used occasionally to brighten sulfur shades or on low-cost bright shades with minimum fastness requirements. For these instances, the following tests are suggested.

If the dyed sample does not bleed, or bleeds only slightly, in the test for direct dye, it should be tested for the presence of a basic dye.

A 100-300 mg sample is placed in a 35 ml test tube, 0.25 to 0.5 ml of glacial acetic acid is added. After warming over a Bunsen burner, 3 to 5 ml of water are added and the mixture is brought to a boil. The sample is removed, 5 to 20 mg of cationic dyeable acrylic fiber or tannin-mordanted cotton is added and boiling continued for 60-80 sec.

Redyeing on acrylic fiber or on tannin-mordanted cotton is evidence of the presence of basic dyes.

Confirmatory Test. If the above bath still contains color after the redyeing has been made, it can be used for the confirmatory test; other-

wise a fresh glacial acetic acid extraction must be made. To this extract is added 5 to 7 ml of 10% caustic soda solution. The mixture is cooled and 3 to 5 ml of ether added. The mouth of the test tube is closed and the tube is shaken well to assure extraction of the basic dye base into the ether layer. The mixture is allowed to separate into layers, and water is added to bring the top of the ether layer to the mouth of the test tube. Part of the ether layer is decanted into a 10 ml test tube, two to five drops of 10% acetic acid are added and the tube is shaken well. The base of any basic dye will leave the ether and appear in the original color in the acetic acid layer.

DIRECT DYES AFTERTREATED WITH RESIN. If the dyed sample failed to bleed or bled but slightly when tested for direct dyes and the test for the presence of basic dyes was negative, investigate the possibility of resin-aftertreated direct dyes.

A 100 to 300 mg sample is placed in a 35 ml test tube, 10-15 ml of a 10% solution of hydrochloric acid is added and boiled for 60 sec. The acid is discarded, a fresh portion added, and the procedure is repeated, followed by a rinse. This treatment removes the resin.

If the sample now bleeds freely in ammonia water and responds fully to the test for direct dyes, then the original dyeing was a direct dye aftertreated with resins.

Group II

Group II includes dyes which change shade on reduction with alkaline sodium hydrosulfite and which revert to the original shade on reoxidation by air: sulfur dyes, vat dyes, aniline and diphenyl blacks.

All samples should be tested for Group I before testing for Group II.

Preliminary Test. A 50 to 100 mg sample is placed in a test tube, 3 to 6 ml of water and 1 to 2 ml of 10% sodium hydroxide are added, and the mixture raised to the boil. Then 10-30 mg of sodium hydrosulfite are added and boiling continued for 2 to 5 sec.

All dyes in this group change shade radically, with the exception of the Indanthrene blues which bleed profusely when the sodium hydrosulfite is added and bleed only slightly or not at all during the caustic soda treatment. The color of the leuco compound of these Indanthrene dyes is blue, differing only slightly in shade from the fully oxidized dye.

The sample is removed and placed on filter paper. All dyes belonging to this group will reoxidize in air to the original shade within 5 to 6 min.

Confirmatory Test For Indanthrene Blues. A ¼-inch square of the cloth sample is placed on several layers of filter paper, wetted with one or two drops of concentrated nitric acid, and the color observed. If the sample turns yellow or green, the sample is blotted with filter paper. If the blot is yellow in color, this blot is touched with a few drops of a re-

duction solution, consisting of equal parts by weight of stannous chloride, concentrated hydrochloric acid and water. The blue color of the original Indanthrene blue will be restored.

SULFUR DYES. A 100 to 300 mg dyed sample is placed in a 35 ml test tube and to it are added 2 to 3 ml of water, 1 to 2 ml of 10% sodium carbonate solution and 200-400 mg of sodium sulfide chips.

The mixture is raised to the boil and boiled 1 to 2 minutes. The sample is removed, and to the test tube are added 25-50 mg of white cotton and 10-20 mg of common salt. After boiling for 1 to 2 min, the cotton sample is removed and placed on filter paper and allowed to reoxidize.

Under these conditions sulfur dyes redye cotton in a shade which differs from the original only in strength. A few, easily reducible vat dyes will color the white cotton, but in a shade markedly different from that of the original dyeing.

Confirmatory Test For Sulfur Dyes. A 100-150 mg portion of the original sample is boiled in 5 ml of 10% sodium hydroxide, rinsed well, and placed in a 15 ml test tube. To it is added 2 to 3 ml of the reduction solution described under the confirmatory test for Indanthrene blue. A piece of filter paper is wrapped over the mouth of the test tube. A small drop of an alkaline solution of lead acetate is placed on the center of the filter paper, and the test tube is placed into a 250 ml beaker containing boiling water. In 40-80 sec, the lead acetate spot on the filter paper will turn dark brown or black if sulfur dyes are present.

Alkaline lead acetate is prepared by adding 10% sodium hydroxide to a 10% solution of lead acetate until the precipitate which is first formed redissolves. To prevent this solution from drying on the filter paper during the test for sulfur dyes, 20-25% of glycerine is added.

Further confirmation may be determined by wetting out the sample with sodium hypochlorite (a 10% concentration of commercial household bleach). The color should be virtually destroyed in 5 min.

VAT DYES, INCLUDING WATER SOLUBLE LEUCO ESTERS. Anthraquinone derivatives generally change very little with 10% hypochlorite. Thioindigo and carbazol derivatives generally lose most of their color in the hypochlorite test and are reduced to a yellow color.

A 100-300 mg dyed sample is placed in a 35 ml test tube to which are added 2 to 3 ml of water and 0.5 to 1 ml of 10% caustic soda solution. After being brought to a boil, a 10-20 mg portion of sodium hydrosulfite is added and boiling continued for another 0.5 to 0.1 min. The sample is removed and 25-50 mg of white cotton cloth and 10-20 mg of salt added. Boiling is continued for 40-80 sec, followed by cooling to room temperature. The cotton is removed and placed on filter paper to oxidize.

Redyeing of cotton to a shade differing only in strength from the

original dyeing indicates the presence of vat colors. This conclusion is valid only if sulfur dyes were ruled out by the preceding test.

OXIDATION BLACKS (ANILINE AND DIPHENYL). Neither of these dyes will redye cotton from sodium sulfide-sodium carbonate treatment or from sodium hydrosulfite-caustic soda treatment.

Confirmatory Test For Oxidation Blacks. A 100-300 mg portion of the dyed sample is placed in a small evaporating dish, 2 to 3 ml of concentrated sulfuric acid poured over the sample and the dish rotated just long enough to extract the dye. The extract is poured into a 35 ml test tube containing 25-30 ml of water, filtered through 5 to 7 cm filter paper and washed several times with water. The side of the paper is spotted with a few drops of 10% caustic soda solution. A red violet spot confirms the test.

Group III

Group III includes the following dyes, which are destroyed in alkaline sodium hydrosulfite and do not redye white cotton from their bleeding in water, water-ammonia or acetic acid: direct dyes aftertreated with metals, direct dyes aftertreated with formaldehyde, naphthols and insoluble azo dyes, and diazotized and developed dyes.

Preliminary Group Test. A 100-300 mg portion of the dyed sample is placed in a 35 ml test tube with 3 to 5 ml of water, 1.5 to 3 ml of 10% sodium hydroxide and 20-40 mg of sodium hydrosulfite. The mixture is brought to a boil and boiled for 3 to 5 min.

All dyes of this group are destroyed; some immediately and some on prolonged boiling.

The destruction of dye is manifested by a permanent change from the original shade to white, grey, yellow, and orange shades. This change takes place both on the sample of cloth and in the extract.

Reoxidation of the sample does not restore the original shade.

DIRECT DYES AFTERTREATED WITH METALS. These metal complexed dyes are recognized by the presence of a metal residue in their ash.

Procedure 1. A sample of approximately 0.5 g is ashed in a porcelain crucible, and the ash melted with four to five times its amount of a mixture of equal parts of sodium carbonate and sodium nitrate. Specific coloration of the cooled melt indicates presence of one of the following metals: copper, faint blue-green; nickel, brown; cobalt, royal blue; manganese, blue-green; chromium, yellow.

Procedure 2. A sample of approximately 0.5 g is ashed in a porcelain crucible. To this is added 2.5-3.0 ml of 30% acetic acid. Specific tests for the presence of copper, nickel, cobalt, manganese or chromium are run immediately as follows.

Copper. A 0.5 ml sample of the acetic acid solution is blended with an equal volume of 10% ammonium thiocyanate solution and a few drops of pyridine. When copper is present, a yellow-green copper-pyridine-thiocyanate complex is formed which is soluble in chloroform.

A second 0.5 ml sample of the acetic acid solution can be mixed with an appreciable excess of ammonia, after which a few drops of a 1% aqueous solution of sodium diethyl-dithiocarbamate are added. A brown precipitate indicates the presence of copper.

Nickel. A 0.5 ml portion of the acetic acid solution is made alkaline with ammonia, and a few drops of a 1% aqueous solution of disodium dimethylglyoxime are added. A red precipitate indicates nickel.

Cobalt. To 0.5 ml of a saturated aqueous ammonium thiocyanate solution is added 0.5 ml of the acetic acid test solution. If cobalt is present, blue cobalt thiocyanate will be formed.

Alternatively, 0.5 ml of the acetic acid test solution may be added to 0.5 ml of a saturated acetone solution of ammonium thiocyanate. A deep blue coloration denotes cobalt.

Manganese. A 0.5 ml sample of the acetic acid is heated, cooled, and a few drops of 10% sodium periodate are added. A characteristic permanganate color formed on warming indicates the presence of manganese.

Chromium. To a 0.5 ml sample of the acetic acid solution are added a few drops of lead acetate solution. A yellow precipitate (lead chromate) indicates chromium.

DIRECT DYES AFTERTREATED WITH FORMALDEHYDE. The presence of formaldehyde in the sample is evidence of the presence of this class of dyes.

Test For Formaldehyde. A sample is heated to boiling in a 5% solution of sulfuric acid and allowed to cool; this extract is added, drop by drop, to 0.1% carbazole dissolved in concentrated sulfuric acid. The formation of a blue precipitate indicates the presence of formaldehyde.

The dyes whose fastness to washing is only slightly improved by aftertreatment with metals or formaldehyde respond to the tests under Group I but their bleeding in dilute ammonia would be insufficient for a good redyeing on white cotton.

NAPHTHOLS AND INSOLUBLE AZO DYES; DIAZOTIZED AND DEVELOPED DYES. These two classes of insoluble azoic dyes are totally different in their properties but related to each other in that the final dye which appears on the material is never present as such in a dyebath but is formed *in situ* on cotton.

In the preparation of diazotized and developed dyes, cotton is dyed with a suitable direct dye which is then diazotized and treated in a developer bath. In this way, a new dye of increased molecular weight is formed on the fiber. Due to the increased size of the molecule, the solu-

bility of this new dye in water is greatly reduced and the product has increased fastness to washing.

In the preparation of naphthol dyes, phenolic compounds possessing an affinity for cotton are first applied and then treated with a solution of stabilized diazonium salts, whereupon a dye is formed *in situ*. Neither of the two parts entering into the formation of the dye possesses water-solubilizing groups, and the dye formed is water insoluble.

In this systematized scheme of identification, these two classes of dyes are placed at the very end of the procedure, when all other possible classes of dyes have been eliminated, and the problem is narrowed down to the question of differentiating between them.

NAPHTHOLS AND INSOLUBLE AZO DYES. The most characteristic property of this class is bleeding in pyridine. A 20-50 mg dyed sample is placed in a 10 to 15 ml test tube, 1 to 2 ml of pyridine added and the sample boiled. All naphthol dyeings bleed to some extent. Due to their water insolubility, naphthols reduce much more slowly in sodium hydroxide and hydrosulfite than any other class of dyes in Group III.

Confirmatory Test. A 100-200 mg dyed sample is placed in a 10 to 15 ml test tube, and 2 ml of 10% sodium hydroxide and 5 ml of alcohol are added. The mixture is boiled, 5 ml of water and 40-50 mg of sodium hydrosulfite are added, and the mixture again brought to a boil. After the color is reduced, the mixture is cooled and filtered. To the filtrate are added 10-20 mg of white cotton and 20-30 mg of salt. This is boiled 1 to 2 min, cooled and the cotton removed. A yellow dyeing which fluoresces in ultraviolet light confirms that the original was dyed with a naphthol or printed with an insoluble azo dye.

DIAZOTIZED AND DEVELOPED DYES. These dyes are identified by exclusion of all other classes of this group. Diazotized and developed dyeings do not bleed in pyridine, and they are reduced readily in boiling sodium hydroxide and sodium hydrosulfite. Some of these dyes might tint pyridine, and for reassurance, the test may be repeated on the same sample with two to three fresh portions of pyridine. The tinting by some of these developed dyes decreases rapidly and in most cases terminates completely. The bleeding in the case of naphthol dyeings continues at the same rate, since solubility is an inherent property of all naphthol dyeings.

Occasionally, part of the dye will be poorly coupled and bleed in water-ammonia in the tests of Group I. This bleeding, however, is only slight and of a different shade than the original dyeing. Redyeing on white cotton is impossible or too poor to warrant placing in the class of straight direct dyes.

Group IV

PIGMENTS. When prior tests for other dye classes on cellulose show negative results, the presence of pigments or fiber reactive dyes should be suspected. Microscopic examination, solvent bleeding and chemical tests can yield information about the presence and the type of resin bonded pigment.

In mass pigmented viscose rayon, pigment particles show uniform distribution throughout the fiber under the microscope. Resin-bonded pigments show surface coloration. The surface coloration is obvious in deep shades but not readily recognized in light shades.

Extraction of the sample with a boiling solvent such as dimethylformamide can be useful in distinguishing between some classes of dyes and as a preliminary test for pigments. Resin-bonded pigments may belong to the azoic, phthalocyanine or vat classes but may also be inorganic substances. The water-in-oil type of resin-bonded pigments, especially the phthalocyanine blue and phthalocyanine green pigments, do not bleed in dimethylformamide, whereas the oil-in-water formulation does bleed.

Microscopic Examination. Samples of fiber may have a starch or resin type finish which should be removed so that they do not interfere with the identification. An enzyme scour with 2% enzyme and 0.25% detergent at 160F for 30 min will remove normal starch finishes. Stripping of the resin may be carried out by treatment with 1% hydrochloric acid for 5 min at the boil, followed by a rinse. A microscopic test may then be carried out by gently removing a few fibers from the sample and untwisting. The fibers are mounted in a drop of ethyl salicylate and covered with a coverslip. A granular appearance of the fiber surface is characteristic of resin bonded pigments.

Dimethylformamide Extraction. The fiber is placed in 5 ml of a 1:1 solution of dimethylformamide and water and brought to a boil, removed from the heat and staining of the solvent observed. Another sample of the fiber is placed in 5 ml of 100% dimethylformamide and the procedure repeated. The degree of solvent staining serves to distinguish between pigments and fiber reactive dyes. If the sample dyed with fiber reactive dyes is not adequately washed, a slight bleeding will be shown in the water-dimethylformamide solution. The solvent staining behaviors of various types of dyes are summarized in Table I.

REACTIVE DYES. Reactive dyes are characterized by a relatively stable chemical combination with the cellulose fiber. This linkage gives the dyeing excellent insolubility in solvents and water. There is no specific unambiguous test for reactive dyes. It is necessary to eliminate the possibilities of other dyes which are fast to water bleeding, e.g. azoic, sulfur, and vat dyes, before seeking to establish the color as a reactive

Table I. Dimethylformamide Staining Test for Dyes

1:1 DMF:Water	100% DMF
Stained by:	Stained by:
All Direct	Vats
Diazotized and Developed	Leuco Vats
Some Basic	Naphthols
Some Mordants	Sulfurs
	Pigments
Not Stained by:	Some Basic
Fiber Reactive	Some Mordants
Leuco Vats	
Naphthols	Not Stained by:
Pigments	Fiber Reactive
Some Basic	
Some Mordants	

dye. It should be noted that pigments resemble reactive dyes in several of the identification tests and that solvent insolubility and behavior with reducing and oxidizing agents are key tests in proving the presence of reactive dyes.

Reagents. Reduction: 5% sodium hydroxide and 5% sodium hydrosulfite in water.

Acetic acid, 5% in water.

Oxidation: 5% hydrogen peroxide or 10% sodium perborate in water.

DMF (dimethylformamide), 100%.

Hypochlorite-sodium hypochlorite bleach containing 2% available chlorine.

Procedure. The sample is placed in slow boiling reduction reagent and the reaction and time of reaction observed. Azoic direct and diazotized and developed dyes decolorize rapidly. Vat, sulfur and aniline black dyes are rapidly converted to the alkaline leuco form. Some red pigments are stripped by this reduction, but the reaction is slow and is easily distinguished from the more rapid cases cited above.

Some fiber reactive dyes containing anthraquinone chromophores will be reduced by the reagent but will seldom be converted to the original shade by oxidation. Others containing an azo chromophore will be decolorized by the reducing reagent and by hypochlorite.

If the test sample is converted to the alkaline leuco form in the reduction reagent, the sample is removed and placed in the acetic acid solution. Vat, sulfur, aniline black and chrome dyes will form an acid leuco compound differing in color from both the original sample and the alkaline leuco compound.

The acid leuco sample may be re-reduced and then placed in the oxidizing reagent. The original shade of the sample should be restored.

The effect of the hypochlorite on the dyed sample is observed after

immersing a fresh sample in the reagent for a few minutes, blotting between paper towels and drying.

Reactive dyes have many kinds of structure, but for reference purposes they may be classified by the kind of group which attaches the dye to the fiber molecule such as the vinyl sulfone, acrylamide, halopyrimidine and halotriazine. Within any series, the dyes may contain different dye chromophores. For example, bright blues can have phthalocyanine or anthraquinone structures. Azo structures with and without metal complexes are common in this group. A detailed discussion of the chemistry of reactive dyes has been given by Venkataraman (2).

Although reactive dyes are attached to the cellulose by primary valencies, certain types e.g. Remazols (vinylsulfones) and Primazins (acrylamides), will hydrolyze when boiled under alkaline conditions (5% sodium hydroxide). The bleeding into the solution may indicate direct dyes, but the hydrolyzed dye will not redye cotton as direct dyes will.

Reduction of fiber reactive dyes can give shade changes similar to those experienced with vat dyes. Phthalocyanine and anthraquinone structures in the fiber reactive dyes are reducible to leuco compounds which will return to the original shade on oxidation.

The procedure for identification of reactive dyes should first eliminate the possibility of vat, sulfur, and azoic dyes. Tests already described should be used after removing any resin from the sample by boiling in a dilute acid solution.

Specific tests for azoic, vat, and sulfurs should be carried out. Azoic dyes are soluble in cold chloroform and give a colored solution when a sample is shaken with this solvent in a test tube. Bright and strongly colored samples of vat dyes suggestive of fiber reactive dyes will bleed in the reduction reagent. Similarly, a dull yellow or orange-colored sample with some color bleeding into the solution indicates a sulfur dye. In both cases, if the reduced sample is washed and exposed to the air, it will return to its original shade. Some reactive blues will give strongly colored reduction products, although the original shade returns much more slowly. These blues can be distinguished from vat dyes since they are decolorized in cold weak sodium hypochlorite, whereas vat dyes are not.

Reactive Phthalocyanine And Anthraquinone Dyes. Phthalocyanine and anthraquinone compounds are reducible to leuco compounds, which in turn can be reconverted to the initial compounds by reoxidation. The reduction-oxidation process should be obvious and reversible, that is, the action of the reducing agent must produce a clearly visible shade change and on oxidation the original shade must be restored. The optimum conditions for this procedure consist of reduction of the specimen for 30 sec at room temperature in a water solution containing 20 g/l. of sodium hydrosulfite and 2.5 g/l. of sodium hydroxide, followed

by 2 min rinsing in cold water, 2 min rinsing in hot and again 2 min in cold water.

Generally, phthalocyanines regain their original shade on rinsing, while anthraquinones do not. Oxidation at 90-95C for 2.5 min will restore the original shade of the anthraquinones.

Reactive Azo Dyes. Dyeings of reactive azo dyes can be reduced to primary amines and decomposed so that the reactive fragment remains linked to the fiber while the amine fragment or fragments can be washed off. Often the primary aromatic amino group of the resulting fiber-linked compound can be diazotized and the diazonium compound combined with a suitable coupling component to give a new reactive dyeing. To carry out this method for demonstrating the presence of a reactive azo dye, the amine bound to the fiber must be diazotizable. A number of cleavage products may be obtained which react with nitrous acid in ways other than the formation of a diazonium compound. The success of this method is therefore contingent upon carrying out the diazotization and coupling under suitable conditions and therefore requires some knowledge of azo dye synthesis.

The presence of reactive dyes may be confirmed by their resistance to bleeding when they are boiled with solvents. A summary of this behavior is included in Table I. Direct dyes can be stripped with mixed solvents such as 57% pyridine-43% water and 50% dimethylformamide-50% water. Azoic dyes will bleed into pyridine and into dimethylformamide. Vat dyes, with some exceptions, are partially stripped by 100% pyridine or dimethylformamide.

With the exception of a few Levafix dyes and certain turquoise blues, reactive dyeings which have been freed of unfixed dye show practically no bleeding when they are treated at the boil for 5 minutes with solvents.

More detailed procedures for identification of reactive dyes can be obtained from the literature (*9-11*).

Dyes On Animal Fibers

A burning test serves to identify wool or silk. These fibers are also differentiated from others by their solubility in boiling 5% sodium hydroxide. The following dye classes are normally used in the dyeing of wool or silk: Basic, Direct, Acid, Soluble Metallized (acid dyeing), Chrome, Metallized (neutral dyeing), Vat, Leuco Ester and Naphthols.

Basic Dyes

A 100-300 mg sample of dyeing is placed in a 35 ml test tube, boiled in 10 ml alcohol for a few minutes and removed. The alcohol solution is evaporated almost to dryness, 5 ml of water added and the mixture

boiled to remove the alcohol. To the residue is added 0.25 to 0.5 ml of 10% sodium hydroxide. After cooling the solution, 5 ml of ether is added and the tube shaken to extract the basic dye. The layers are allowed to separate, the ether layer decanted into a 10 ml test tube and a few drops of 10% acetic acid are added with shaking. The salt form of the basic dye which results should have the original color of the dyed sample.

Additional proof of the presence of basic dyes may be obtained by placing a sample of mordanted cotton or cationic dyeable acrylic fiber in the test tube with the alcohol extract, adding the sodium hydroxide and transferring the dye to these new fibers.

Direct Dyes

A 100-300 mg sample of dyeing is placed in a 35 ml test tube, 5 ml of water and 1 ml of concentrated ammonia are added and the sample is boiled in this solution for 1-2 min. The dye sample is removed, and 30 mg of salt and 10-30 mg of white cotton are added. Boiling is continued for 1 to 2 min. The cotton is removed and rinsed.

If a direct dye is present the cotton will be dyed a deep shade. Some acid dyes may stain cotton, but never to a deep shade.

Acid Dyes

The procedure to be used is essentially the same as that for direct dyes (above), but instead of adding salt, the ammonia is neutralized with a 10% sulfuric acid solution, and a few drops of acid are added in excess. A 20-40 mg piece of wool is added, and the mixture boiled for 1 to 2 min. Redyeing of the extracted dye on wool from this acid bath is evidence of the presence of acid dyes.

This test is significant only if the previous test on redyeing of cotton and the following test for soluble metallized dyes have been carried out. Positive evidence of direct cotton dyes and acid dyes indicates a union dyeing on a blend of wool and cotton.

Soluble Metallized Dyes ("Acid Dyeing")

The procedure to be used is identical with the method given above for acid dyes. Soluble metallized dyes are distinguished by the presence of chromium in the ash.

The procedure for the determination of metals is described in the section dealing with direct dyes on cellulosic fibers.

Chrome Dyes

Chrome dyes are formed *in situ* on wool by treating a chromium-

wool complex with a water soluble dye. The resulting chrome dye is not soluble in water, and the procedure recommended above for acid dyes will not extract any dye. However, the procedure may produce considerable bleeding into the dilute ammonia. No redyeing of wool can be accomplished from this extract because it contains by-products of the dyeing process which were not removed prior to finishing.

Some further evidence for chrome dyes can be obtained from the ash test discussed below.

Metallized Dyes (Neutral Dyeing)

The dye-metal complexes are preformed and are exhausted from the dispersion onto wool. Due to the poor solubility of these organometallic complexes in water, only small amounts of dye can be extracted from a sample of a dyeing. Redyeing of wool by such an extract does take place however, in distinction from the results of this test with chrome dyeings, but the shade is always much lighter than the original shade.

Ash Test for Metallized Dyes. Neutral metallized dyes may contain either chromium, cobalt, or manganese. When either of the last two metals is found in the ash of a sample, metallized dyes are immediately suspected because chrome color dyeings invariably contain chromium only. A dyeing produced with a neutral dyeing chromium metallized dye always contains less chrome than chrome dyes.

To carry out the test ash, 20 mg of dyed sample is placed in a No. 000 porcelain crucible and 500 mg of sodium carbonate-sodium nitrate mixture added. The mixture is fused, allowed to cool and examined. If the color of the flux is yellowish, a chrome dye is indicated. If the flux is white, then the sample probably contained a neutral dyeing chromium metallized dye. The validity of the test is dependent on the positive test for chrome when a larger sample (300-500 mg) of this dyeing is used.

Vat Dyes

A 200-300 mg sample is placed in a 35 ml test tube, 2.5 ml of 10% sodium hydroxide added, and the mixture boiled until all of the wool is dissolved. To the wool solution are added 25-50 mg of sodium hydrosulfite, 10-15 mg of white cotton and 25-50 mg of salt. The test tube is heated to near boiling for 1-2 min and cooled to room temperature. The cotton is removed and placed on filter paper for 1-2 min, then in an oxidizing bath containing sodium nitrite and acetic acid. Development of a color on the cotton is evidence of vat dyes.

If the original sample was dyed in a light shade, the redyeing on cotton will be too faint and it is necessary to repeat the dyeing of the same piece of cotton with several 200-300 mg samples of the original.

Vat dyeing made in the past may contain traces of chromium due to

the industrial practice of reoxidation of vat dyeings with sodium dichromate, but the quantity usually found is not significant. Occasionally indigo, or solubilized vat blue, and chrome colors may be dyed on the same cloth. In this case, the analyst will detect the two classes of dyes. The vat component can be redyed on cotton by the procedure given above, which will destroy chrome dyes. The vat component can be completely removed by repeated extractions with pyridine leaving the chrome color intact on the sample.

Leuco Esters

These are water soluble, stable esters of vat dyes. When they are used to dye wool fiber, they are saponified and oxidized, producing a true vat color which can be identified with the above procedure for vat dyes.

Naphthol Dyes

These are water insoluble azo dyes formed on the fiber *in situ*. Their presence on the sample is determined by the exclusion of all other classes of dye and by the fact that naphthol dyeings bleed freely in pyridine. In addition they are reduced by sodium hydroxide-sodium hydrosulfite to a yellow, orange shade, incapable of reoxidation.

The procedure for the identification of naphthol dyes is detailed in the section dealing with cellulosic fibers.

Dyes On Man-Made Fibers

Fiber Identification

The solvent scheme used for the identification of acetate, triacetate, polyamide, acrylic or polyester fibers may also give hints as to the nature of the dye present on a particular fiber. The procedure suggested here is based on the exclusion principle, and Table II summarizes the sequence of solvents used (*11*).

Dyes On Cellulose Acetate Or Cellulose Triacetate

Solubility in cold acetone identifies secondary acetate. In a mixture of 80% acetone and 20% water, secondary acetate dissolves immediately, whereas the triacetate becomes translucent and tender but retains its fiber form.

The following dye classes are used in the dyeing of both of these fibers: disperse, acid, basic, vat, developed, pigments (co-spun or resin-bonded).

Appreciable quantities of acetate fibers are marketed with co-spun

Table II. Solubility of Man-Made Fibers in Various Solvents

Fiber	Soluble	Insoluble
Sec. Cellulose Acetate	Acetone/Water, 80/20, Cold Benzyl Alcohol (50C)	
Cellulose Triacetate	Methylene Chloride, Cold	Acetone/Water, 80/20, Cold Benzyl Alcohol (50C)
Polyamide	85% Formic Acid, Boiling	Dimethylformamide, Boiling Acetone, Cold Methylene Chloride, Cold
Nylon 6	Dimethylformamide/Formic Acid (85%), 75/25, Boiling	Cyclohexanone
Nylon 66		Dimethylformamide/Formic Acid (85%), 75/25, Boiling Cyclohexanone
Nylon 11	Cyclohexanone	
Acrylic	N-Methylpyrrolidone, Boiling Dimethylformamide, Boiling	Acetone, Cold Methylene Chloride, Cold
Polyester	N-Methylpyrrolidone, Boiling	Acetone Cold Methylene Chloride Dimethylformamide, Boiling

pigments. For the most part, the dyeing of acetate fibers is with disperse dyes.

The diazotized and developed dyes are usually blacks and occasionally navies.

An overall indication of the type of dye present may be obtained by the following color transfer test and by solvent extraction.

A 100-300 mg sample is placed in 25 ml of a soap solution (5 g/l.) with an equal weight of undyed acetate fabric and warmed at 90C for 10 min. The color of the solution, the change in color of the original and the degree of color transferred to the undyed acetate are noted.

The soaping test gives a clear indication of fibers dyed with disperse dyes. Disperse dyes will transfer to the undyed acetate to give appreciable color. No transfer is observed with pigmented fibers. Basic dyes will transfer from the acetate fibers to the soap solution but will not redye the acetate. Azoic combinations will give only a light yellow on the acetate derived from uncoupled intermediates. The absence of staining on the acetate fiber does not rule out acetate fibers which have been dyed with acid dyes or vat dyes. These dyes will not redye the acetate to any significant extent.

The extraction test with N-methylpyrrolidone followed by distribution of the extracted dye between the toluene and water layer serves to distinguish among the possibilities in water soluble dyes.

A 100-300 mg sample is placed in a 35 ml test tube and 5 ml of a 25% solution of N-methylpyrrolidone added. The test tube is immersed

in a water bath and the temperature of the bath is raised to boiling. After 20-40 sec, the tube is removed and the dyeing discarded. To the solution 3-5 ml of toluene and 20 ml of water are added. The tube is shaken well and the color of the water layer and the toluene layer noted.

DISPERSE DYES. If the extraction test yields a toluene layer which is strongly colored, the dye is most likely a disperse dye. Confirmation is made by separation of the toluene layer in a separatory funnel. The toluene is evaporated and the residue dispersed in water with a surfactant, e.g., lignin sulfonate (Marasperse N). A redyeing on acetate fabric is evidence of disperse dyes.

ACID DYES. If the extraction test results in a water layer which is strongly colored and the same shade as the original dyeing and a colorless toluene layer, then the dye may be an acid dye.

Confirmation is made by treating a new sample with 10 ml of 5% sodium hydroxide at the boil for 2 min. The sample is removed and an equal quantity of undyed wool is added. Dilute sulfuric acid is added to a pH of 4.5 to 5.0 and warmed to 90C. An acid dye will color the wool under these conditions.

BASIC DYES. If basic dyes are present, the water layer and the toluene layer in the extraction test may both be colored. If a basic dye is suspected, a new sample should be extracted by heating in 5% formic acid solution at 90C for 10 min. If the extract redyes cationic dyeable acrylic fiber, the presence of basic dyes is indicated.

VAT DYES. The extraction test gives colorless water and toluene layers with vat dyes. However, the lack of color may also be due to developed acetate dyeing or co-spun pigments.

A 100-300 mg sample of a dyeing is placed in a 35 ml test tube and 1 to 2 ml of 20% sodium hydroxide solution added. After boiling the sample for 1 to 2 min, 4 to 8 ml of water and 15 to 35 mg of sodium hydrosulfite are added, and boiling continued for another 0.5 to 1 min. The sample is removed, and a 25-50 mg piece of white cotton and 15-30 mg of salt are added. Boiling is continued for 40-80 sec and then the mixture is allowed to cool to room temperature. The cotton is removed and placed on filter paper to oxidize by air.

Redyeing of cotton by the above procedure to a shade differing from the original dyeing only in strength indicates the presence of vat colors.

DEVELOPED DYES. Developed dyes may be suspected if the N-methylpyrrolidone extract is colorless or colored a different shade than the original dyeing — usually a shade of brown — no matter what the original shade was. The water and toluene layers are colored; in some cases coloration of the toluene is stronger, in other cases the water. The coloring is different in shade from the original dyeing, and it is usually light brown.

Further differentiation between azoic and vat dyes may be made by reduction. A sample is warmed at 60C with 10 ml of 5% sodium hydroxide to which are added 5 ml of Cellosolve and 50 mg of sodium hydrosulfite. Vat dyes are reduced to leuco compounds, which are different in color from the original dyeing but return to the original color on exposure to air. If no change in color is noted at 60C, heating to the boil decolorizes azoic dyeings.

PIGMENTS. The presence of pigments is indicated by the exclusion of other types of dyes and through their failure to redye any fibers. Pigments vary in their chemical nature, and no specific tests can be given. Blacks are carbon blacks and do not decolorize in sodium hydroxide and hydrosulfite. The presence of metals in the ash is indicative of the use of co-spun pigments.

Confirmation is by microscopic examination previously described in the section on pigments.

Dyes On Polyester Fibers

Polyester fibers are distinguished by their insolubility in boiling 85% formic acid. Boiling nitrobenzene dissolves polyester fibers of both types, disperse- and cationic dyeable. Polyacrylonitrile fibers are insoluble in boiling nitrobenzene. Boiling N-methylpyrrolidone dissolves polyester and polyacrylonitrile fibers.

Polyester fibers are hydrolyzed completely by boiling for a few minutes with $2N$ sodium hydroxide in methanol. A clear solution is obtained when the reaction product is diluted with water. On addition of dilute sulfuric acid, the resulting terephthalic acid separates out as a precipitate.

The following dye classes are used for polyester: disperse, developed, cationic, pigments (co-spun or resin bonded), vat.

IDENTIFICATION OF DYESTUFF CLASSES. A 3 to 5 g portion of caprolactam is melted in a 50 ml test tube over a small Bunsen flame and 100-300 mg of the dyed polyester is dissolved in the molten mass while being stirred with a glass rod. To this is added sufficient (3 ml) ethanol to prevent the caprolactam from solidifying. After cooling the material below 35C, it is diluted with 15 ml of ether and filtered. If the ethereal solution is colored, it is extracted twice with 20-30 ml of water to remove the caprolactam, 2-3 g of sodium sulfate being added to prevent the formation of an emulsion.

The ethereal layer is transferred to a 35 ml test tube and 10 ml of water together with a few drops of a 10% solution of dispersing agent, (e.g., Marasperse N) are added. The ether is evaporated by boiling the solution on the water bath and 100 mg of white acetate fabric is added to the aqueous dye dispersion, which is then kept for 10 min in the water bath.

The formation of an intense coloration of the acetate fabric in the same shade as the original polyester material indicates the presence of disperse dyes. The formation of a slight coloration indicates the presence of developed dyes or vat dyes.

In the latter case, the acetate fabric is removed, and the hot dye dispersion treated with 3 ml of 1N sodium hydroxide and a few milligrams of sodium hydrosulfite and shaken. If the color disappears or changes and the original shade does not reappear on shaking with air, then developed disperse dyes of the azo type have been used to dye the polyester. Vat dyes are reoxidized to the original shade by shaking with air.

If the polyester material has been dope-dyed with pigments or has been dyed with basic dyes, then the ethereal extract of the molten caprolactam is practically colorless, and the precipitated polyester on the filter is strongly colored. Another sample of the dyed polyester material is boiled for 1 min with glacial acetic acid, the solution is evaporated on the water or steam bath and the residue is dissolved in 5 ml of water. A piece of cotton mordanted with tannin or a piece of acrylic fabric is then added, and the liquid is boiled for 1 min. Basic dyes transfer to the fabric. Pigments can be recognized by the fact that the glacial acetic acid extract is colorless or that the residue on evaporation is insoluble in water. Cross-sections of dope-dyed fibers show a uniform pigment distribution when examined under the microscope.

Dyes On Acrylic Fibers

Acrylic fibers consist primarily of polyacrylonitrile and may be classified by the minor component with which the acrylonitrile is copolymerized. The cationic dyeable and acid dyeable types represent the major types. Modacrylics, which contain proportionately more copolymer, represent the minor type.

Acrylic fibers are identified by their insolubility in boiling 85% formic acid and by their solubility in boiling N-methylpyrrolidone. They can be differentiated from polyester fibers by their insolubility in nitrobenzene or o-cresol.

The following dye classes are used in the dyeing of acrylic fibers: disperse, metallized acid (neutral dyeing), basic, acid and chrome.

SEPARATION OF ACRYLIC FIBER DYES INTO GROUPS. Dyes for acrylic fibers can be separated into two major groupings on the basis of solubility, as shown in Table III. The procedure is as follows.

A 100-300 mg sample is placed in a 35 ml test tube and 2 ml of 40% aqueous solution of N-methylpyrrolidone added. The test tube is placed in a beaker of boiling water for 10-20 min or until a sufficient amount of dye has bled into the reagent. An alternative solvent which will extract

cationic or acid dyes is a 57/43 mixture of pyridine and water. The test tube is removed from the water bath, the fiber sample discarded, and the extract poured into a 15 ml test tube containing 10 ml of toluene. After shaking, 1 ml of water is added, and the test tube shaken again. The test tube is allowed to stand until two layers are well separated. The distribution of dyes in the two layers is as given in Table III.

Table III. Distribution of Dyes Used for Acrylic Fibers

Toluene Layer	Water Layer
All Disperse Dyes	All Basic Dyes
Some Neutral Dyeing	All Acid Dyes
Premetallized Dyes	All Chrome Dyes
	Some Neutral Dyeing
	Premetallized Dyes

Disperse And Neutral Metallized Dyes. The toluene layer contains only two classes of dyes — disperse dyes and neutral dyeing metallized acid dyes which contain no or very few water solubilizing groups in their molecules.

The presence of chromium, cobalt, or manganese in the ash of the original dyeings differentiates these metallized dyes from the disperse dyes, which contains no heavy metals.

For a confirmatory test, the toluene layer can be separated by means of a small separatory funnel, washed with water and evaporated. The residue is dispersed with a drop of 10% water solution of a dispersing agent such as Blancol. The dispersion can be used to redye wool and acetate. Metallized dyes will dye wool only. Disperse dyes will dye wool and acetate. Acetate is usually dyed heavier.

The aqueous layer contains basic, acid or metallized acid dyes. Simple tests can differentiate them.

Basic Dyes. A 2 ml portion of 10% sodium hydroxide solution is added to the toluene solution obtained in the previous test. The test tube is placed in a beaker of boiling water for a few minutes, removed, cooled, shaken and the two layers allowed to separate.

A major portion of the toluene layer is decanted into a 10 ml test tube and 0.5 ml of 10% acetic acid is added. The tube is shaken and allowed to stand. A basic dye will color the lower acid layer in the shade of the original dyeing.

Acid Dyes. If the ash of the original dyeing contains no heavy metal and if basic dyes have been excluded, an acid dye is indicated.

Metallized Acid Dyes (Neutral Dyeing) And Chrome Dyes. The ash of the original dyeing is examined for the presence of cobalt, manganese or chrome. When cobalt or manganese are found, the dyeing was probably made with metallized neutral dyeing acid dyes. When chromium is

present, a distinction between chrome colors and neutral dyeing metallized dyes is made by semiquantitative determination of the amount of chrome present in the ash. The procedure suggested in the section dealing with wool dyes may be used.

Remarks. There are a few basic dyes which may cause a misinterpretation of the results of the toluene extraction. These dyes are of the Chrysoidine and Bismark Brown types and are used mostly for compounding black shades. They color the toluene layer and have an affinity for acetate fibers. Therefore, when the sample is dyed a black shade and its main constituents are basic dyes, one should not look for an acetate color as a component of this black dye but ascribe the yellow coloring of toluene to the presence of Chrysoidine or Bismark Brown.

Dyes On Nylon

Nylon fibers are differentiated from other fibers by solubility characteristics as outlined in Table II. The following dye classes are used in the dyeing of nylon: disperse, direct, acid, basic, neutral metallized, acid metallized, chrome, logwood, naphthol, vat, and reactive disperse dyes of the Procinyl type.

In order to get a general indication of the types of dye present on a nylon sample, the following preliminary tests should be carried out: a wash test, followed by redyeing on multifiber cloth, an ash test for determination of metals, and a solubility test for distribution in water or toluene layer.

Wash Test. A 200-300 mg sample of the original dyeing is placed in a 35 ml test tube, and 10-15 ml of a solution composed of 0.50% neutral soap and 0.20% sodium carbonate is added. The test tube is placed in a beaker of boiling water for 15-30 min, then removed from the water; the nylon sample is discarded. Half of this wash test solution is decanted into another 35 ml test tube. To one tube is added 1-2 ml of glacial acetic acid. Then a 3/8 to 1/2 inch strip of Multifiber Fabric No. 5* is added to each test tube, both test solutions are boiled for 3-5 min. The dyeings are rinsed well, and which fibers are dyed and stained on both the alkaline redyeing and the acid redyeing is noted.

Ash Test. The presence of metallized dyes is determined by the analytical procedure already described for direct dyes aftertreated with metals.

Solubility Test. A 100-300 mg sample of the original dyeing is placed in a 35 ml test tube, 15 ml of 57/43 pyridine/water (bp 95C) added, and the tube placed in a beaker of boiling water and boiled 15-30 min. Extractions with pyridine should be carried out in a hood. All classes of

*Multifiber Fabric No. 5 can be obtained from Testfabrics Inc., 200 Blackford Ave., Middlesex, N.J. 08846 and contains the following fibers: acetate, Acrilan 1656, Arnel, cotton, Creslan 61, Dacron 54, Dacron 64, nylon 66, Orlon 75, silk, Verel A, viscose, and wool.