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THE DYEING OF DACRON WITH
METAL-COMPLEX COMPOUNDS

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THE DYEING OF DACRON WITH
METAL-COMPLEX COMPOUNDS

Approved: _____

Date Approved by Chairman: September 5, 1959

DEDICATION

To my wife and daughter

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SUMMARY

The purpose of this work was to investigate the possibility of using metal-complex compounds to dye hydrophobic fibers in an aqueous dyebath without the use of dyeing assistants or temperatures above the boil.

Five organic compounds -- catechol, 2-nitroso-1-naphthol, alizarin, salicylic acid, and ethylenediamine tetraacetic acid -- were used as chelating agents. The compounds were reacted with metallic salts of iron, copper, cobalt, zinc, tin, nickel, silver, and chromium in attempts to obtain a colored complex which would penetrate and dye Dacron* fiber. The in situ formation of the complex was attempted as was the application of the preformed complex to the fiber.

Several colored compounds were found to be capable of dyeing Dacron. Of these, a complex of catechol and iron (from ferric chloride) when applied to the fiber by a one-bath method showed the greatest promise. This product, when applied to Dacron, possessed satisfactory light fastness and fair washfastness. The fact that full penetration could be obtained in as little as two hours without the addition of chemical assistants to the aqueous dyebath, was of particular interest; temperatures above the boil were not required.

Alizarin and 2-nitroso-1-naphthol were also found to

*This is du Pont's trademark for its polyester fiber.

possess interesting dyeing properties when applied to Dacron in the pH range of 1.0 - 5.0. The fastness properties of these compounds when reacted with various metals were not of sufficient merit to meet the requirements of the dyeing trade.

Attempts to use salicylic acid or ethylenediamine tetraacetic acid coupled with various metallic salts proved unsuccessful as dyes for Dacron.

This empirical investigation did not produce a product which could immediately be adapted for practical dyeing; however, an approach for future research in the dyeing of hydrophobic fibers was introduced.

CHAPTER I

INTRODUCTION

Since man first began to dye textile fibers, he has been faced with many dyeing problems. The synthetic dye chemist continues to develop new and better dyes and to improve the fastness properties of the dyes already in use. There are still many unsolved problems existing in the dyeing of natural fibers.

The introduction of synthetic fibers to the textile industry presented serious problems to the dyer. In an effort to obtain outstanding tensile strength and dimensional stability, the synthetic fiber producers subject these fibers to stretching and heat setting which produces a dense, impermeable structure into which a dye molecule has difficulty penetrating (1).

The synthetic fibers, such as Dacron, Orion, Dynel, Acrilan, polyethylene and Saran, possess the desirable characteristics of tensile strength, elasticity, economy, crease resistance, abrasion resistance, and resistance to chemicals. High chemical resistance, one of their most valuable properties, magnifies the disadvantage of poor dyeability with existing dyes. In addition, their hydrophobic character, limited swelling properties, and smooth surfaces make penetration and retention of dye particles by absorption

extremely difficult (2).

Synthetic fibers can be divided into two groups. There are those, such as Saran and polyethylene, which contain no obvious sites for dye absorption; and those such as Dacron and Orlon, which contain sites but have such a compact physical structure that dye diffusion within the fiber is very slow (1). Information from X-ray diffraction studies has indicated that Dacron possesses a neatly-packed, zig-zag pattern of long chain molecules. There are no gaps to suitably accommodate the dyestuff molecules, and the fiber molecules are very reluctant to change their position or to lose their orientation. Consequently, the dyestuff molecules do not easily penetrate the fiber as indicated by the fact that days or even weeks are necessary to dye a Dacron fiber at a temperature of 85°C (3).

The successful dyeing of fibers without sites can only be effected through modification of the structure of the fiber. Even those hydrophobic fibers with sites have a compact structure which resists swelling in aqueous dyebaths and hinders the diffusion of the dye molecule into the fiber. The problem of dyeing is therefore one of slow diffusion rather than lack of dyeing sites, as shown by Waters in his experiments with Terylene (4). There are three avenues of approach to increase the rate of diffusion of the dye within the impermeable, site-possessing fiber: to use dyes of small molecular size, to use swelling agents to increase the

permeability, and to use high dyeing temperatures (5).

The disperse dyes, which were developed for dyeing cellulose acetate, have been found to have an affinity for Dacron and other hydrophobic fibers. It has been suggested that linkage between the dye and the fiber is due to hydrogen bonding, dipole interaction, or van der Waals forces (6). The disperse dyes are relatively simple molecules, the benzene-azo-benzene type being the smallest known (7). Studies of the effect of dye structure on dyeing rates have established a practical size limit beyond which dyeing rates are too slow. Even though good shade depth can be obtained at equilibrium with some disperse dyes, the larger ones do not produce satisfactory shades within the normal time of a practical dyeing (8). The fastness to dry heat-sublimation is also a problem with many disperse dyes, 1, 4-dihydroxyanthraquinone for example, showing some color removal by simple ironing (9).

The difficulty found in dyeing synthetic fibers made it necessary to resort to other means which would provide adequate depths of shades. One of these techniques employs assistants, or "carriers", which may be one of several classes of chemicals (10). A variety of organic hydrocarbons, substituted hydrocarbons, phenols, amines, acids, amides, alcohols, esters, etc., is used to accelerate the rate of dyeing of disperse dyes on hydrophobic fibers at temperatures up to 212°F (11). In spite of the disadvantages such as toxicity,

stream pollution, high cost, and unpleasant odor, dyeing with carriers is generally preferred for production dyeing (12). Advantages claimed for the use of carriers in aqueous dyeings are increase in total absorption of dye, improvement in the leveling or transfer during dyeing and attainment of better fastness properties especially to washing and sublimation (13). Although some of the newer dyeing assistants perform fairly well, the perfect carrier is yet to be developed. The ideal carrier should be odorless, nonvolatile, nonflammable, nontoxic, water soluble, inexpensive, effective in low concentration and easily removable after dyeing (14). Until such time as the perfect dyeing assistant is devised, carrier dyeing is only a temporary expedient which enables hydrophobic fibers to be dyed, with some degree of success, in equipment originally intended for some other fiber where temperatures above the boiling point are not required (15).

A more recent trend in the dyeing of synthetic fibers is the use of temperatures above 212°F. In all dyeing processes, an increase in temperature is known to accelerate the rate of dyeing by increasing the mobility of the polymer chains in the amorphous regions of the fiber and the movement of the dye molecules. Experiments with Orlon dyed with acetate dyes have shown that more color is absorbed when dyeing with 1.0 per cent of dye at 250°F than when dyeing with 5.0 per cent of dye at 203°F. An increase in the absorption of vat

and acetate dyes by Dacron is also effected by the use of temperatures as high as 250°F (16). Dyeing at temperatures above the boiling point without carriers has advantages in that the expense of the carrier and necessity for its removal after dyeing are avoided (12). High-temperature dyeing involves more costly machinery. It is nevertheless generally preferred for dyeing staple fiber or yarn, while carrier dyeing is used more widely on piece goods. A method called the "Thermosol" process has been developed by which high temperatures can be reached in dyeing Dacron fabric (17). The use of higher temperatures shows great promise for the future dyeing of the hydrophobic fibers. The high cost of machinery remains the main problem to be overcome.

It is felt that disperse dyes, carriers, and high temperatures are only temporary means by which the hydrophobic fibers may be dyed and that they were developed in order to satisfy the demands of the industry. As the synthetic fibers become more entrenched in the field of textiles, the question remains: can the problem of dyeing the compact hydrophobic fibers be solved by synthesis of new dyes?

The use of metallic salts in the field of textile dyeing is hundreds of years old. Metals have found extensive use as mordants in dyeing. Chromium is used today in the dyeing of wool and nylon to improve the lightfastness and washfastness of the dye. The metal-complexed dyes are applied

by several methods: the metallic salt is applied first and the dye second; the dye is applied first, and the metal second; the metal and the dye are applied together; or the metal is complexed with the dye and then applied to the fiber.

There are certain organic compounds called chelating agents, that are capable of forming colored complexes with metals. Examples of these chelating agents, which have oxygen as electron donors, are alizarin, gallic acid, salicylic acid, catechol, etc. Many literature references can be found discussing the use of these compounds in forming colored compounds and solutions when complexed with various metals. No information has been found, however, referring to their use in the dyeing of the man-made, hydrophobic fibers.

The purpose of this investigation was to explore the possibility of using metal-complex compounds in the dyeing of hydrophobic fibers. Because of the small molecular size of these compounds, it was felt that perhaps they would penetrate the compact structure of these most difficult-to-dye fibers; and once complexed either in situ, or before application to the fiber, would be fast to light and laundering.

Experiments were conducted under various conditions, using several chelating agents and several metallic salts. The in situ formation of colored complexes was attempted, as was the application of preformed complexes to the fiber. No chemical assistants to swell the fibers, or temperatures above 212°F, were used.

CHAPTER II

EXPERIMENTAL PROCEDURE

Preparation of Fabric Samples.--The fabric samples used in this investigation consisted of 1.5 inch staple, 3 denier per filament Dacron in the form of knitted tubing. Before dyeing, the Dacron was scoured for 20 minutes at 160 - 180°F in a bath containing 2.0 per cent, based on weight of fiber (owf), anionic Tergitol and 2.0 per cent (owf) ammonium hydroxide (28%), then rinsed with tap water. Water was periodically added during the scouring to maintain a 40:1 bath to fiber ratio.

Chemicals Used.--All chemical compounds were weighed accurately on an analytical balance and dissolved in deionized water. The chemicals used (listed below) were reagent grade with the exception of the surface active agents.

- alizarin
- catechol
- ethylenediamine tetraacetic acid, disodium salt
- ethylenediamine tetraacetic acid, tetrasodium salt
- 2-nitroso-1-naphthol
- sodium salicylate
- chromic chloride
- cobaltous chloride
- cupric sulfate
- ferric chloride
- nickelous sulfate
- silver nitrate
- stannic chloride
- zinc sulfate

acid acetic
sulfuric acid
ammonium hydroxide
sodium carbonate
alkylaryl polyglycol (Tergitol nonionic NPX, anhydrous)
sodium heptadecyl sulfate (Tergitol anionic 7)
flake soap

General Dyeing Procedure.--All samples were dyed under reflux conditions with the exception of those used for light and washfastness tests; these were dyed in open beakers in which the bath to fiber ratio was maintained constant by the addition of water (deionized water was used throughout the dyeing procedure except for rinsing which was done with tap water). The baths were constantly agitated with glass rods by hand. The samples were entered at the boil, and dyeing was continued at 212°F for the specified time interval.

Aftertreatment of Samples.--The soaping treatment following each dyeing was done in a 40:1 bath containing a 2.0 per cent soap solution. The samples were treated for 5 minutes at 160° - 180°F, then rinsed for one minute with water.

Experiments with Catechol and Ferric Chloride -- Two-Bath Method.--This method involved the treatment of Dacron with catechol and ferric chloride in separate baths. A 1.0 gram Dacron sample was boiled for 2 hours in a 40:1 bath containing 10.0 per cent (owf) catechol. After being rinsed with water the sample was then boiled for 2 hours in a 40:1 bath containing 10.0 per cent (owf) ferric chloride, then rinsed with water, soaped, rinsed again, and air dried.

A similar experiment was performed using 20.0 per cent (owf) catechol and 20.0 per cent (owf) ferric chloride. The original experiment was repeated using a 10.0 per cent catechol solution and a 10.0 per cent ferric chloride solution.

The two-bath method was reversed by boiling 1.0 grams Dacron first for 2 hours in 40.0 ml of a 10.0 per cent ferric chloride solution, rinsing with water, and then boiling for 2 hours in 40.0 ml of a 10.0 per cent catechol solution.

Experiments with Catechol and Ferric Chloride -- One-Bath

Method.--This method consisted of treating the Dacron at the boiling point in a bath containing both catechol and ferric chloride. A 1.0 gram Dacron sample was boiled for 2 hours in a 40:1 bath containing 20.0 ml of catechol solution and 20.0 ml of ferric chloride solution, rinsed with water, soaped, rinsed again, and air dried. Several concentrations of the catechol and ferric chloride solutions were combined as follows:

Per Cent Solutions of		
	Catechol	Ferric Chloride
Bath 1	10.0	10.0
Bath 2	10.0	5.0
Bath 3	10.0	2.5
Bath 4	5.0	10.0
Bath 5	5.0	5.0

It was decided to use a dispersing agent in the bath, and to add the complexing agents on a mole to mole basis. A 40:1 bath was prepared containing 20.0 ml of a 0.5 M catechol solution, and 0.25 grams per liter Tergitol, nonionic. The

bath was brought to the boil and a 1.0 gram sample of Dacron was entered. The dyeing was continued for 2 hours at the boiling point. The Dacron sample was removed, rinsed with water, soaped, rinsed again, and air dried.

In order to check the effect of concentration, the preceding experiment was repeated using 0.25 M solutions of catechol and ferric chloride, and then 0.125 M solutions. The mole ratio of catechol to ferric chloride in both cases was 1:1.

The effect of time of dyeing was checked by dyeing Dacron as before using 0.5 M catechol and ferric chloride solutions. The dyeing was continued at the boil for 2, 3, 4, 5, and 6 hours. Cross sections of the fibers were made and examined under the microscope.

To determine optimum dyebath pH, several dyeings were conducted (using 0.5 M solutions) at different pH's. The pH of the baths (preformed complex) was adjusted with sulfuric acid or sodium hydroxide. The pH of the catechol-ferric chloride complex (1:1), as formed, was 0.7. Dyeings were conducted at pH 0.5, 0.7, 1.5, 3.0, and 5.0.

Light and washfastness tests were run on a 6.0 gram Dacron sample dyed by the one-bath method using equal portions of 0.5 M solutions of catechol and ferric chloride.

Experiments with Catechol and Cupric Sulfate.--The two-bath method was repeated using cupric sulfate. A 1.0 gram sample

was boiled for 2 hours in 40.0 ml of a 10.0 per cent catechol solution, rinsed with water, then boiled for 2 hours in 40.0 ml of a 10.0 per cent cupric sulfate solution. This procedure was repeated in reverse, i.e., the Dacron was treated with the cupric sulfate first and the catechol second.

Using the one-bath method, 1.0 grams Dacron was boiled for 2 hours in a bath consisting of 20.0 ml of 0.5 M catechol solution, 20.0 ml of a 0.5 M cupric sulfate solution, and 0.25 grams per liter nonionic Tergitol. The sample was rinsed with water, soaped, rinsed, and air dried. The series of experiments was performed using different pH's. The cupric sulfate was first added to the catechol and the pH of the bath was adjusted with sodium hydroxide or sulfuric acid. Dyeings were conducted at pH 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0. A 6.0 gram sample was dyed by this method at pH 6.0, and fastness tests were run.

Experiments with Catechol and Other Metals.--An investigation was made using catechol combined with various other metals. The metallic salts used were silver nitrate, chromic chloride, stannic chloride, zinc sulfate, cobaltous chloride, and nickelous sulfate.

The two-bath method was tried first. The Dacron was boiled for 2 hours in a 10.0 per cent solution of catechol, rinsed, and boiled for 2 hours in a 10.0 per cent solution of the metal. Each of the above named metals was used in this

series of experiments. The two-bath method was repeated in reverse by treating the Dacron with the metal first, and catechol second.

The one-bath method was then tried with each of the above metal compounds. All dyebaths were 40:1, containing 20.0 ml of a 0.5 M catechol solution, 20.0 ml of a 0.5 M solution of the metal and 0.25 grams per liter of nonionic Tergitol. The treatment was continued for 2 hours at the boiling point. This experiment was repeated, at different dyebath pH using each of the metals. After the bath was prepared, the pH was adjusted with sodium hydroxide or sulfuric acid. Dyeings were run at pH 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0.

Experiments with 2-Nitroso-1-Naphthol and Various Metals.--A 0.05 M solution of 2-nitroso-1-naphthol was prepared by dissolving the compound in deionized water with sufficient sodium hydroxide added to effect dissolution. The pH of this solution was 11.5. Since it was found that in the pH range 1.0 - 5.0 2-nitroso-1-naphthol had a great affinity for Dacron, dyeings were conducted using this compound only in order to set a shade standard. A 1.0 gram Dacron sample was boiled for 2 hours in 40.0 ml of a 0.025 M solution of 2-nitroso-1-naphthol containing 0.25 grams per liter of nonionic Tergitol. The pH of the bath was adjusted at room temperature to 1.0 with sulfuric acid before the dyeing was begun. The experi-

ment was repeated using different pH's. Acetic acid or sulfuric acid (for pH below 3.0) was used for the pH adjustments.

A 6.0 gram sample was dyed as outlined above at a dye-bath pH of 1.0 and fastness tests were run.

Experiments were then conducted with 2-nitroso-1-naphthol and ferric chloride. A bath was prepared by adding 20.0 ml of a 0.05 M ferric chloride solution to 20.0 ml of a 0.05 M solution of 2-nitroso-1-naphthol. Nonionic Tergitol was added until a 0.25 gram per liter concentration was obtained. Immediately upon the addition of the ferric chloride, the bath turned black. This was interpreted to mean that a complex was formed. The pH of the bath was 2.2. Sulfuric acid was added at room temperature until the pH was 1.0. A 1.0 gram Dacron sample was boiled in this bath for 2 hours, rinsed with water, soaped, rinsed again, and air dried. The experiment was repeated at pH 1.0, 2.0, 3.0, 4.0, and 5.0. Acetic acid or sulfuric acid (for pH 1.0 - 3.0) was used for the pH adjustment. The experiment was repeated with a 6.0 gram Dacron sample (at pH 1.0) and fastness tests were conducted.

The above experiment was repeated using 0.05 M solutions of chromic chloride and 2-nitroso-1-naphthol. When the chromic chloride solution was added to the 2-nitroso-1-naphthol solution, the bath turned milky yellow. The pH of the bath

was 5.0. Dyeings were conducted in the pH range of 1.0 - 5.0. Again acetic or sulfuric acid was used for the pH adjustments. All baths remained yellow until they were brought to the boil, at which time they turned dark maroon. One gram samples were entered and boiled in the baths for 2 hours. This experiment was repeated with a 6.0 gram sample dyed at a dyebath pH of 1.0, and fastness tests were conducted.

A bath was made up containing 20.0 ml of a 0.05 M nickelous sulfate solution, 20.0 ml of a 0.05 M solution of 2-nitroso-1-naphthol, and 0.25 gram per liter nonionic Tergitol. The nickelous sulfate and 2-nitroso-1-naphthol formed a dark orange solution having a pH of 7.0. The pH was lowered to 5.0 with acetic acid. The dyebath was brought to the boil and a 1.0 gram sample was entered. Dyeing was continued at the boil for 2 hours. The sample was rinsed with water, soaped, rinsed again, and air dried. The experiment was repeated several times, dyeing in the pH range of 1.0 - 5.0. Acetic acid or sulfuric acid (for pH below 3.0) was used for the adjustments, and it was observed that at pH 1.0 - 2.0, the solution darkened. The experiment was repeated with 6.0 gram Dacron samples dyed at pH 1.0 and 4.5 and fastness tests were conducted.

Experiments were conducted with 2-nitroso-1-naphthol and the following metallic salts: silver nitrate, stannic chloride, zinc sulfate, cobaltous chloride, and cupric sulfate.

The procedure as outlined in the preceding experiment was followed. For all dyeings the 2-nitroso-1-naphthol and metal were combined mole to mole. Dyeings were conducted in the pH range of 1.0 - 5.0 with each of the above metals.

Experiments with Alizarin and Various Metals -- Two-Bath

Method.--Alizarin solutions were prepared by dissolving the alizarin in deionized water with sufficient sodium hydroxide added to effect dissolution.

The two-bath method consisted of first treating the Dacron with alizarin, and then treating the sample in a bath containing a metal solution. The metallic salts used for these experiments were silver nitrate, ferric chloride, stannic chloride, zinc sulfate, nickelous sulfate, cobaltous chloride, chromic chloride, and cupric sulfate. The first step involved boiling the 1.0 gram Dacron sample for 2 hours in a 40:1 bath containing 2.0 per cent (owf) alizarin and 0.25 grams per liter of nonionic Tergitol. The dyebath pH was lowered to 3.0 with acetic acid before entering the Dacron sample. The sample was removed, rinsed, and boiled for 2 hours in a 40:1 bath of a 5.0 per cent solution of the particular metal. The sample was then rinsed with water, soaped, rinsed again, and air dried.

Experiments with Alizarin and Various Metals -- One-Bath

Method.--A 0.005 M solution of alizarin was prepared by dissolving the alizarin in deionized water and sufficient sodium

hydroxide. Solutions (0.005M) of stannic chloride, zinc sulfate, silver nitrate, nickelous sulfate, cobaltous chloride, ferric chloride, chromic chloride, and cupric sulfate were prepared. Experiments were conducted with alizarin and each of the above mentioned metals. The pH of 20.0 ml of a 0.005 M solution of alizarin was adjusted to 1.0 and 20.0 ml of a 0.005 M solution of the particular metal was added. Sulfuric acid was used for the pH adjustment. Nonionic Tergitol was used in the bath in the concentration of 0.25 grams per liter. A 1.0 gram Dacron sample was entered at the boil, and dyeing was continued at that temperature for 2 hours. The sample was then rinsed, soaped, rinsed and air dried. The experiment was repeated several times with other alizarin solutions, the pH of which ranged from 1.0 to 9.0 (in steps of one).

A 0.6 gram sample was dyed (at pH 1.0) by this method using 0.05 M solutions of alizarin and ferric chloride. Fastness tests were conducted on this sample as well as one dyed with a 0.025 M solution (pH 1.0) of alizarin only.

Experiments with Salicylic Acid and Various Metals -- Two-Bath Method.--Solutions of sodium salicylate were prepared by dissolving the compound in deionized water.

A preliminary experiment was conducted using the sodium salt (sodium salicylate) as a chelating agent rather than free salicylic acid. A 1.0 gram Dacron sample was boiled for 2 hours

in 40.0 ml of a 10.0 per cent sodium salicylate solution. The sample was rinsed, and then boiled for 2 hours in 40.0 ml of a 10.0 per cent ferric chloride solution. After the sample was placed in the ferric chloride solution, the bath turned dark purple. The experiment was repeated using 10.0 per cent solutions of stannic chloride, zinc sulfate, silver nitrate, nickelous sulfate, cobaltous chloride, chromic chloride, or cupric sulfate.

Experiments were then conducted with (free) salicylic acid in attempts to dye Dacron. A bath was prepared using 40.0 ml of a 10.0 per cent sodium salicylate solution into which a 1.0 gram sample was entered. The bath was heated to 180°F. With the temperature held constant at 180°F, sulfuric acid was added slowly until the dyebath pH was lowered to 1.0 (as indicated by pH hydrion paper). The sample was boiled in the free salicylic acid for 2 hours, rinsed in water, and placed in 40.0 ml of a 10.0 per cent ferric chloride solution. The dyeing was continued at the boil for 2 hours. As before, the ferric chloride solution turned deep purple when the sample was entered. The experiment was repeated with each of the above named metallic salts.

The two-bath method was repeated in reverse with each of the above metallic salts. The Dacron sample was boiled for 2 hours in a 10.0 per cent solution of the metal, rinsed, and placed in a bath containing a 10.0 per cent sodium salicylate

solution. The salicylic acid was freed as before by holding the bath temperature at 180°F and adding sulfuric acid until the pH was to 1.0. Dyeing was continued for 2 hours at the boiling point.

Experiments with Salicylic Acid and Various Metals -- One-Bath Method.--In this experiment, attempts were made to dye Dacron with the preformed complex of salicylic acid and metal from the following salts: ferric chloride, stannic chloride, zinc sulfate, silver nitrate, nickelous sulfate, cobaltous chloride, chromic chloride, and cupric sulfate.

A 1.0 gram Dacron sample was placed in 40.0 ml of a 0.25 M sodium salicylate solution. The temperature was raised to 180°F and sulfuric acid was added slowly at that temperature, until the pH of the bath was 1.0. Once the salicylic acid was freed, the reaction was continued at the boil for 10 minutes, after which 20.0 ml of a 0.5 M solution of the metal was added. Dyeing was continued at 212°F for 2 hours. Ferric chloride and salicylic acid formed a deep purple solution. Cupric sulfate and salicylic acid formed a milky white solution. The dyebaths to which stannic chloride, silver nitrate and zinc sulfate were added, remained clear. The dyebaths to which the remaining metals were added were colored the same as the particular metallic salt solution.

Experiments with EDTA and Various Metals -- Two-Bath Method.--

A 1.0 gram sample of Dacron was placed in 40.0 ml of a 10.0

per cent solution of the disodium salt of ethylenediamine tetraacetic acid (EDTA), the pH of which had been lowered to 3.0 with acetic acid. The sample was boiled in this solution for 2 hours, rinsed, and placed in 40.0 ml of a 10.0 per cent ferric chloride solution. Dyeing was continued at the boil for 2 hours. This experiment was repeated using 10.0 per cent solutions of cobaltous chloride, chromic chloride, cupric sulfate, and nickelous sulfate. A 1.0 gram Dacron sample was boiled for 2 hours in 40.0 ml of a 10.0 per cent solution of the disodium salt of EDTA. The pH of the bath had been adjusted to 3.0 with acetic acid before the sample was entered. The Dacron was then rinsed and boiled for one-half hour in 40.0 ml of a 1.0 per cent solution of sodium hydroxide. The sample was then rinsed again and boiled for 2 hours in 40.0 ml of a 10.0 per cent ferric chloride solution. This experiment was repeated with each of the metal salts used previously.

Experiments with EDTA and Various Metals -- One-Bath Method.--

Attempts were made to dye Dacron with a complex formed from EDTA and metallic salt solutions. The metals used were the same as those in the preceeding experiments with the two-bath method. Dyeings were done with each metal combined with EDTA solutions of different pH values. In each dyeing the pH of the EDTA solution was adjusted with acetic acid before the metal was added. Solutions of the tetrasodium salt of EDTA

were prepared with pH ranging from 3.0 to 9.0 (3.0, 4.0, 5.0, etc.). The dyeings were conducted as follows: a 1.0 gram sample of Dacron was boiled for 2.0 hours in a 40:1 bath containing 20.0 ml of a 0.05 M solution of the tetrasodium salt of EDTA and 20.0 ml of a 0.05 M solution of the metal.

Colorfastness to Light.--Throughout the procedure, mention was made of Dacron samples dyed for fastness tests. These samples were tested for light-fastness according to the American Association of Textile Chemists and Colorists Standard Test Method 16A-1957 (18), and evaluated on the basis of the number of clock hours required to cause just appreciable fading.

Colorfastness to Washing.--Certain of the dyed Dacron samples were tested for washfastness according to the American Association of Textile Chemists and Colorists Standard Test Method 36 - 1957 (19). The samples were rated by comparing with the standard grey scale.

Table I. Fastness Properties of Colored Compounds on Dacron Polyester Fiber

Compound	pH of Dye bath	Color Obtained	Light (Fade-Ometer) ³ Hours to Cause Fading	Wash (Launder-Ometer) ⁴ Rating
Catechol and FeCl_3 ¹	0.7	Dark Grey	Approximately 40	2
Catechol and CuSO_4 ¹	6.0	Light Grey	Approximately 30	2
2-Nitroso-1-Naphthol (only) ²	1.0	Dark Brown	Approximately 5	4-5
2-Nitroso-1-Naphthol and NiSO_4 ¹	1.0	Reddish Brown	Approximately 5	4-5
2-Nitroso-1-Naphthol and NiSO_4 ¹	4.5	Orange	Approximately 10	2
2-Nitroso-1-Naphthol and FeCl_3 ¹	1.0	Light Brown	Approximately 5	4-5
2-Nitroso-1-Naphthol and CrCl_3 ¹	1.0	Reddish Brown	Approximately 5	4-5
Alizarin (only) ²	1.0	Bright Yellow	Over 60	5
Alizarin and FeCl_3 ¹	1.0	Greenish Yellow	Over 60	3

1. Complex preformed and applied by one-bath method

2. Used for color standard

3. AATCC Test Method 16A-1957 (18)

4. AATCC Test Method 36 - 1957, Test No. 3 (19)

CHAPTER III

RESULTS AND DISCUSSION

The primary objective of this work was to develop a product which would dye Dacron in aqueous dyebaths without using dyeing assistants or temperatures above 212°F. The secondary objectives were to obtain maximum penetration, depth of shade and fastness properties.

Experiments with Catechol and Ferric Chloride.--Preliminary experiments revealed that ferric chloride and catechol formed a dark, black solution which indicated that a complex was formed. Attempts to dye Dacron by forming the complex in situ (two-bath method) failed. Although the Dacron was stained, for all practical purposes the fibers were not dyed. It is believed that the failure was due to the fiber's inability to absorb the iron molecules as they existed alone and uncomplexed in the dyebath. This belief is based on information given on the Eastofix process which involves the application of metalizable dyes to cellulose acetate followed by the padding on of a metal-containing fixing salt (20). It is interesting to note that in the development of this Eastofix process, padding was the only means by which the metallic fixing salt could successfully be applied to the fiber (20). Boiling Dacron in a ferric chloride solution after the fiber

had first been treated with catechol in a separate bath, caused a gradual darkening of the dyebath. This suggests that perhaps the catechol molecules were leaving the fiber and forming a complex with iron molecules in the bath.

Experiments with the one-bath method proved successful in the coloring of Dacron. A series of dyeings was conducted in baths of different concentrations (page 9). All of the samples were dyed grey. The most promising result was obtained from Bath 1 (page 9) which contained equal portions of 10.0 per cent solutions of catechol and ferric chloride. The sample from this bath was dyed the darkest shade. The preformed complex seemed to form insoluble particles in the bath, which were deposited on the surface of the sample. At this point it was decided to use a dispersing agent in the bath and to combine the complexing agents on a mole to mole basis.

The best results were obtained with mole to mole combinations of catechol and iron. It was observed that at lower concentrations, the Dacron was dyed a lighter color. The shade ranged from a dark blue-black obtained with the 0.5 M solutions, to a light grey with the 0.125 M solutions. Dyeings conducted for different lengths of time produced similar shades on the Dacron. The shade depth on the fibers varied very little between the two and six hour dyeings. Cross sections of the fibers revealed that full dye penetration was

obtained after dyeing for two hours. Further dyeings with this preformed complex at different pH's gave the following results:

<u>pH of Dyebath</u>	<u>Result</u>
0.5	Sample dyed dark blue black
0.7	Sample dyed dark blue black
1.5	Sample dyed light blue grey
3.0	Sample dyed light grey
5.0	Sample dyed very light grey

The best shades were obtained at pH values below 1.0. In all of the baths a black deposit was left on the flasks and on the surface of the Dacron. It is believed that the catechol-iron complex, when applied to the Dacron, behaved similarly to disperse dyes.

The fastness properties of Dacron dyed by the one-bath method were not good (page 21). The sample faded after approximately 40 hours exposure in the Fade-Ometer; the wash rating was 2 (poor). The Dacron may have retained an excess of uncomplexed catechol. This supposition is based on the fact that catechol solution, when exposed to light, deteriorates and turns dark. As stated previously, there were dark, insoluble particles present on the fiber surface which were removed during the soaping operation causing the shade of the Dacron to be lighter. The poor wash rating possibly resulted from the incomplete removal of these particles.

Experiments with Catechol and Cupric Sulfate.--Results similar to those with ferric chloride were obtained with catechol and

cupric sulfate. Again the two-bath method proved unsatisfactory, but the one-bath method showed promise. Catechol and cupric sulfate, when combined in a mole ratio of 1:1, formed a dark complex which dyed the Dacron grey. Dyeings with this complex at different pH values indicated that the optimum pH for a stable complex to be formed is somewhat higher than the pH at which iron will complex with catechol. It was observed that the higher the pH, the darker the shade on the Dacron. At pH 1.0, the sample was not colored while at pH 5.0, the sample was dyed grey. The catechol-copper complex also appeared to be water insoluble and again a dispersing agent was used in the bath. The Dacron sample which was dyed at pH 6.0, had a wash rating of 2 and faded after approximately 30 hours exposure in the Fade-Ometer. (See Table I, page 21.) The fair lightfastness could again be attributed to excess catechol, and the poor washfastness to incomplete removal of the particles on the surface of the fibers.

Experiments with Catechol and Other Metals.--Attempts to dye Dacron with catechol complexed with silver, chromium, tin, zinc, cobalt, or nickel, did not produce encouraging results. The fiber was not dyed with any of the compounds by either the one or two-bath method. No color was imparted to the Dacron treated with chromic chloride, zinc sulfate, cobaltous chloride, or nickelous sulfate. Samples treated with silver nitrate and stannic chloride were slightly stained. Treat-

ments were conducted in the pH range of 1.0 - 5.0. The negative results of these experiments did not justify further investigation.

Experiments with 2-Nitroso-1-Naphthol and Various Metals.--

It was found that 2-nitroso-1-naphthol would completely penetrate and dye Dacron in the pH range 1.0 - 5.0. Shades obtained on the fiber with this compound alone were as follows:

<u>pH of Dyebath</u>	<u>Shade</u>
1.0	Maroon
2.0	Brown
3.0	Olive
4.0	Olive
5.0	Olive

However, the colors obtained with this compound possessed poor lightfastness properties as shown in Table I (page 21).

It was thought that if 2-nitroso-1-naphthol could be complexed with a metal (1:1) and applied to the fiber, that the fastness properties could be improved. Experiments were first conducted with iron at various pH values. The results were as follows:

<u>pH of Dyebath</u>	<u>Result</u>
1.0	Sample dyed dark brown
2.0	Sample dyed light tan
3.0	Sample not colored
4.0	Sample not colored
5.0	Sample not colored

As compared to the fastness properties of Dacron dyed with 2-nitroso-1-naphthol only, the iron complex (at pH 1.0) yielded essentially the same results -- good washfastness and

poor lightfastness (Table I, page 21).

Similar experiments were then conducted with chromium, the results of which were:

<u>pH of Dyebath</u>	<u>Result</u>
1.0	Sample dyed dark reddish brown
2.0	Sample dyed maroon
3.0	Sample dyed light maroon
4.0	Sample dyed light maroon
5.0	Sample dyed light maroon

The fastness properties of 2-nitroso-1-naphthol were not improved by the chromium.

The experiments with nickel proved very interesting. The 2-nitroso-1-naphthol and nickelous sulfate, when combined mole to mole, formed a dark orange solution. As the pH of this solution was lowered, the color changed to dark maroon. Dyeings at different pH values gave the following results:

<u>pH of Dyebath</u>	<u>Result</u>
1.0	Sample dyed dark reddish brown
2.0	Sample stained blotchy purple
3.0	Sample dyed uneven orange
4.0	Sample dyed light orange
5.0	Sample dyed light orange

The 2-nitroso-1-naphthol-nickel complex (at pH 1.0) did not show any improved fastness properties. However, it was interesting to note that nickel, when complexed with 2-nitroso-1-naphthol at pH 4.5, showed a slight improvement in lightfastness and a decrease in washfastness (Table I, page 21). Experiments with silver, tin, and zinc yielded essentially the same shades as those obtained previously with 2-nitroso-

1-naphthol alone. Dyeings with cobalt produced a purple stain on the fiber. Dacron samples dyed with copper and 2-nitroso-1-naphthol in the pH range of 1.0 - 2.0, were colored the same shade as those dyed with 2-nitroso-1-naphthol only. The samples treated in the pH range 3.0 - 5.0 were stained, but for all practical purposes, undyed.

Experiments with Alizarin and Various Metals.--Alizarin was found to possess a great affinity for Dacron when used at a low pH (1.0 - 3.0). The fiber was dyed a very bright yellow with excellent wash and lightfastness properties (Table I, page 21). Very even dyeings were effected with the use of a dispersing agent. Microscopic examination (cross section) showed full penetration of the fiber when dyed with low concentrations of alizarin. The alizarin solution changed color as the pH was changed. At pH 11.5 the solution was dark purple, and at pH 1.0, light yellow. It was hoped that alizarin could be complexed with various metal ions to produce different colors on the fiber with good fastness properties.

The in situ formation of a colored product was not accomplished with alizarin and metals. As stated previously, this was probably due to the difficulty Dacron has in absorbing metal ions. With the exception of iron, metals combined with alizarin (one-bath method) did not produce a color different from that obtained with alizarin alone. The Dacron was dyed yellow in all of the baths in which the pH of the

alizarin was 1.0 - 3.0. From pH 3.0 - 5.0, the samples were lightly stained and from pH 5.0 - 9.0, practically no color was imparted to the fibers. Dyeing with ferric chloride and alizarin, combined in a mole ratio of 1:1, produced a greenish-yellow color on the fiber. The washfastness of this product proved to be worse than alizarin alone (Table I, page 21). Excess iron left on the surface of the fiber may have caused the poor rating.

Experiments with Salicylic Acid and Various Metals.--Salicylic acid is known to have the ability to penetrate Dacron, as proved by the fact that it is used as a carrier. In this investigation, salicylic acid was combined with several metals (1:1) in attempts to develop a colored solution that could be used as a dye for Dacron. Iron was the only metal that formed a colored solution when coupled with salicylic acid. When the ferric chloride solution was added to salicylic acid, the bath immediately turned dark purple. This colored compound had no affinity for Dacron, and all attempts to dye the fiber by the one or two-bath method failed. It is believed that after complexing with the iron, the salicylic acid lost its affinity for the Dacron. The investigation was not continued.

Experiments with EDTA and Various Metals.--Ethylenediamine tetraacetic acid is one of the strongest chelating agents used today. When combined with colored metallic salt solutions, this compound will intensify the color. The metals used were

iron, cobalt, chromium, copper and nickel. These were chosen because each forms a colored solution. EDTA, however, showed no interesting dyeing properties when complexed with these metals. Experiments were conducted at various dyebath pH using EDTA and colored metallic solutions combined in a mole ratio of 1:1. It was hoped that the optimum pH for a stable complex would be found and that the complex would dye Dacron. The one and the two-bath method proved unsuccessful. The ferric chloride-EDTA complex stained the fiber slightly, but did not dye it. Negative results were also obtained with cupric sulfate, nickelous sulfate and chromic chloride. Although a slight yellow stain was present on the Dacron treated with EDTA (at pH 3.0 - 4.0) and cobalt, the samples treated at pH 5.0 - 9.0 were left undyed and unstained. Because of the negative results, the investigation was not continued.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated that Dacron can be dyed with certain metal-complex compounds. Colored products with interesting dyeing properties were obtained from complexes of catechol with ferric chloride and cupric sulfate. In addition, 2-nitroso-1-naphthol, when complexed with chromium, iron, and nickel, showed promise as a dye for Dacron. Alizarin, when coupled with iron was found to have an affinity for Dacron fibers.

Throughout this work the failure to form colored products in situ was attributed to the inability of the Dacron to absorb the metal ions. Only the one-bath method, which consisted of applying the preformed complex to the substrate, succeeded in dyeing Dacron.

Of all the experiments described in Chapter II, the one-bath method of applying the preformed complex of catechol and iron proved the most promising. It was found that this product would fully penetrate Dacron in a relatively short period of time.

It is recommended that further study be made of iron and catechol complexes under various dyeing conditions. The two-bath method should be investigated further with emphasis

on other ways to apply the metal, i.e., padding.

Once a method has been devised to apply the metal, the experiments with alizarin, and 2-nitroso-1-naphthol using the two-bath method should be repeated. The excellent fastness properties obtained when Dacron was dyed with alizarin indicate that work with this compound should be continued. Dyeings should be made with simple derivatives of alizarin in an attempt to increase the range of colors obtainable.

Further work with other organic compounds capable of forming colored compounds is recommended. Other metallic salts should be used. The possibilities along this line are unlimited and the success depends on finding the right compounds and the proper conditions necessary to apply them to the fiber.

The possibility of improving the fastness properties of the products used in this work also should be investigated. A reduction clearing operation (such as used with some dispersed dyes) should be included in the procedure to remove the particles which adhered to the fiber surface (21).

Although this investigation did not produce a compound with excellent fastness properties which could be used in practical dyeing, certainly a new approach toward dyeing hydrophobic fibers in an aqueous dyebath has been introduced.

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