

**A NEW METHOD FOR PRODUCING TWO-COLOR
AND TWO-TONE EFFECTS ON WOOL FABRICS**

A THESIS

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Georgia Institute of Technology**

**In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Textiles**

By

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September 1956

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**A NEW METHOD FOR PRODUCING TWO-COLOR
AND TWO-TONE EFFECTS ON WOOL FABRICS**

Approved:

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D. Jack Davis

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.	ii
LIST OF TABLES	iv
SUMMARY.	v
 CHAPTER	
I. INTRODUCTION.	1
History of the Problem	
Purpose of the Research	
Method of Attack	
II. THEORETICAL CONSIDERATIONS.	5
Structure of Wool	
Selection of Wool Dyes	
Forces of Dyeing	
Dyeing Wool with Acid Dyes	
Effect of pH in Wool Dyeing	
Wool Reserve Agents	
Effect of Temperature in Wool Dyeing	
III. INSTRUMENTATION AND EQUIPMENT	15
IV. EXPERIMENTAL PROCEDURES	16
Preliminary Tests and Preparation for Dyeing	
Dyeing the Samples	
V. DISCUSSION OF RESULTS	26
VI. CONCLUSIONS	32
VII. RECOMMENDATIONS	33
BIBLIOGRAPHY	34
APPENDIX	37

LIST OF TABLES

Table	Page
1. Yarn Number, Run, and Cut of Undyed Woolen Yarn.	38
2. Twists per Inch of Undyed Woolen Yarn.	39
3. Characteristics of Dyes Used	40
4. Breaking Strength Determination of Undyed Woolen Fabric (Warp)	42
5. Breaking Strength Determination of Undyed Woolen Fabric (Filling).	43
6. Degradation of Wool by Phosphoric Acid and Synthraton ACA when Dyed with Milling Yellow NOS (6.0 percent) and Alizarine Sapphire FS (2.0 percent) (Warp)	44
7. Degradation of Wool by Phosphoric Acid and Synthraton ACA when Dyed with Milling Yellow NOS (6.0 percent) and Alizarine Sapphire FS (2.0 percent) (Filling)	45
8. Degradation of Wool by Phenol and Synthraton ACA when Dyed with Milling Yellow NOS (6.0 percent) and Alizarine Sapphire FS (2.0 percent)	46
9. Degradation of Wool by Phenol and Synthraton ACA when Dyed with Milling Yellow NOS (6.0 percent) and Alizarine Sapphire FS (2.0 percent)	47

Several recommendations for additional work which would elucidate the nature of the reactions involved in this method, and improve the effects achieved have been included.

CHAPTER I

INTRODUCTION

The inherent properties of wool have enabled the woolen industry to produce fabrics that possess valuable and distinct characteristics. Research is now directed toward means for improving these fabric characteristics.

History of the Problem.--Many fundamental studies of wool are designed to find out how wool performs its function as well as it does. The chemistry of wool is extremely complex. This complexity happens to fit in with the very complex requirements we make on apparel fabrics, but it also makes it extremely difficult to elucidate completely wool's chemical structure. We know that wool is composed of approximately 18 different amino acids; however, we do not know just how these amino acids are arranged within the structure.

Despite this lack of knowledge of the chemistry of wool certain chemical modifications have been devised which produce desired effects in the dyeing operation. Many of these chemical modifications are termed "resist" processes. Hartley, Wood, and Lund (1) have defined a resist process "as one which modifies a textile fibre in such a way that when it is subsequently dyed it takes up less dye or takes up dye more slowly than an untreated fibre."

The limitation of the known resist processes is that they cannot be used on a commercial scale without adverse side effects. Interest in

resist processes for dyeing wool increased notably when Kenwood Mills Limited (2) released for publication the results of a new and undisclosed method, devised in their research laboratory, for dyeing wool blankets two shades in one dyebath.

Hartley, Wood and Lund (3) have published an appraisal of the resist processes available for use on wool. According to their article there are:

" . . .two main ways in which the dyeing behavior of textile fibres may be modified. Firstly, the internal structure may be made more accessible (e.g. by acid chlorination (4) in the case of wool) or alternatively, the fibre may be made less accessible by depositing within it insoluble substances which provide a physical barrier to the entry of dye particles. Secondly, the chemical groupings in the fibre molecules which are known to provide sites for fibre-dye combination may be either reduced in number or supplemented by similar groupings. Reduction in the number of dye-attracting groupings (which may often be accompanied by the introduction of dye-repelling groups which have the same effect on dye uptake) results in the treated material being dyed less deeply than untreated material when both are present in the same dyebath; increasing the number of dye-attracting groups has the opposite effect."

Nine resist processes were mentioned by Hartley, Wood and Lund (5) which were based on the chemical modification of dye-attracting amino-groups and, in certain instances, on the introduction of dye-repelling acidic groups.

Purpose of the Research.--The production of novelty effects by piece dyeing means cheaper production costs and greater flexibility, since the choice of color can be left to the last possible moment and the immediate requirements of the market more easily satisfied. A further advantage is that longer runs in the early stages of processing are possible, and no colored waste is produced.

A cheap, effective and reliable resist process is, however, an absolutely essential first requirement. It must be allied to careful choice of dyes to be used during the subsequent dyeing, and particularly to strict control of the dyeing operation to enable reproducible results to be obtained. The processes developed so far show that moderate, and in certain instances, very good resists may be obtained with wool on a laboratory scale. The development of bulk scale processes is, however, a much more difficult matter. In addition to producing an effective resist, the process must be cheap, reproducible, easily controlled, and must not have adverse side effects on the wool.

Waddington (6) has concluded that, of the methods he examined, alkaline chlorination was the most promising, since it was likely to prove simpler, easier to run and cheaper than the others. On the other hand, it did not give as good a resist as the much more expensive and technically difficult process of acetylation (7). It is known, however, that very few of the methods which are available are yet well established on a commercial scale at an economic price, and even the processes found to be interesting on a laboratory scale have certain serious limitations.

Method of Attack.--It was believed that a satisfactory resist process could be obtained by employing the proper combination of the following factors:

1. pH of the samples of wool to be dyed
2. pH of the dyebath
3. Dyestuffs (selection of dyes of desired dyeing characteristics)
4. Time

5. Use of retarding or resist agents
6. Temperature
7. Use of salt

CHAPTER II

THEORETICAL CONSIDERATION

Any critical examination of the methods of dyeing, and the properties of dyed textile materials requires that consideration be given to the nature of the fibre to be dyed, the dyestuffs used, and the forces which may act to bind the dyestuffs to the fibre.

Structure of Wool.--Proteins have long been recognized as being among the most important substances present in plants and animals. They are found sometimes as individual large molecules with possible molecular weights from 10,000 into the millions. They are also frequently found as a reticular constituent of cells, forming their structural framework.

Conveniently, proteins may be divided into two groups, fibrous and globular. The structure of the fibrous type has been studied the most and is the best characterized. Since proteins are involved in physiological reactions the problem of the structure of proteins is a very important one. However, the investigation of the nature of proteins is attended by many difficulties. Their sensitivity and the ease with which proteins may have their chemical and physical properties changed (denaturation) seriously limits techniques applicable to their study.

The investigation of the structure of fibrous proteins has been limited to either (a) a physical investigation of the intact fibre or (b) an analytical investigation of the amino acid mixture obtained by hydrolysis. In the physical examination of the intact fibre, the

method of x-ray diffraction has yielded results of the utmost importance. From the x-ray diffraction patterns the fibrous proteins have been classified into two groups: (i) the keratin-myosin-fibrinogen group (the k.m.f. group) and (ii) the collagen group.

Most of the proteins from the k.m.f. group give x-ray diffraction patterns closely related to that of natural, unstretched, mammalian hair (alpha-keratin). These fibres, in the manner of alpha-keratin, can be stretched on soaking in hot water or dilute alkali to about double their normal length, giving the stretched beta-keratin form. When so extended, these proteins give x-ray patterns of another somewhat simpler type closely related to that of beta-keratin. Thus the k.m.f. group has subgroups of alpha-, and beta-keratin types.

The collagen group of fibrous proteins does not stretch, though it contracts markedly on soaking in hot water. These proteins give closely-related x-ray patterns which are quite distinct from those of the keratin-myosin types.

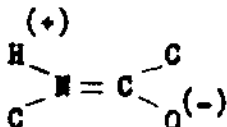
Since the research of Emil Fischer it has been known that proteins are built from alpha-amino acids, to form polypeptide chains of the type:



Pauling, Corey, and Bronson (8) and Pauling and Corey (9) have set out conditions for a satisfactory polypeptide structure:

1. All amino acid residues are equivalent, save for differences in the side chain R.

2. The $\text{H}-\overset{\cdot\cdot}{\text{N}}-\overset{\text{C}_\alpha}{\text{C}}=\text{O}$ is always planar because of resonance with



3. Bond lengths and bond angles of the polypeptide linkage are stated.

4. Every $\text{C}=\text{O}$ group and every $\text{N}-\text{H}$ group is involved in $\text{O} \cdots \text{H}-\text{N}$ bonding with an $\text{O} \cdots \text{N}$ distance of 2.72 \AA , the $\text{O} \rightarrow \text{N}$ vector being within 30° of the $\text{N}-\text{H}$ bond direction.

M. Kehren states (10):

"...when freed from impurities and foreign matter, clean wool fibre consists of carbon, hydrogen, oxygen, nitrogen, and sulphur. The proportion of these elements in the wool molecule is not fixed but varies within narrow limits depending on the breed of sheep and on the conditions under which the wool was grown. Elementary analysis of wool yields the following average percentages:"

<u>Element</u>	<u>Percent</u>
Carbon	50.0 - 52.0
Hydrogen	6.7 - 7.5
Oxygen	22.0 - 25.0
Nitrogen	16.0 - 17.0
Sulphur	3.0 - 4.0

Selection of Wool Dyes.--Dyeing is one of the major finishing operations applied to wool, and may be carried out on loose material, slubbing, yarn, and woven or knitted goods. Selection of dyestuffs and of the dyeing procedure to be employed is largely decided by the end-use of the finished goods and the stage of manufacture at which dyeing is carried out.

The following classes of dyes are applicable to wool, each group representing a virtually complete range of colors:

1. Acid dyes (applicable from a strongly, moderately, or weakly acid dyebath)
2. Chrome dyes (applied by the chrome mordant, afterchroming, and one-bath methods)
3. Chrome complex dyes applied from a strongly acid dyebath
4. Neutral or weakly acid-dyeing chrome or other metal-complex dyes
5. Vat dyes
6. Direct (substantive) dyes

Since the acid dyes was the only class of dyes used in this work the remainder of this discussion will summarize the attempts to classify these dyes according to their behavior and chemical constitution.

Vickerstaff (11) has grouped the acid dyes into three classes (levelling, milling and supermilling) based on their levelling power, method of application, and wet fastness of the final dyeing. He states that these three properties of acid dyestuffs are interrelated and depend upon the fundamental attributes of anion affinity, electrical charge and diffusion rate into the fibre. The "Acid dyes" are mostly sodium salts of sulphonic acids and are dissociated to the free color-acids in an acid dyebath.

Speckman (12) has made the following studies on acid dyes:

1. Relationships between chemical constitution and colloid character
2. Relationship between colloid character, chemical constitution, and levelling capacity

3. Relationship between chemical affinity and levelling capacity

No attempt was made to classify the dyes as a consequence of these studies, but Speakman did note the effect of their molecular weight, affinity, and number of sulphonic acid groups, on dyeing wool with various defects.

Townsend and Simpson (13) have reported an extensive investigation into the relationship between dyeing behavior and the chemical constitution of the dyes. These authors studied mainly the dyeing of normal and dry chlorinated wool and found that contrast effects can be produced with many direct cotton and milling acid dyes. Level dyeing acid dyes, however, produce little or no contrast, but Townsend (14) found that by the addition of wool reserve agents to the dyebath, it is possible to produce contrast effects with these dyes also.

Townsend divided the level dyeing acid dyes into four subdivisions: the non-contrast producing group; and three contrast producing groups. An examination on the basis of the contrast produced (on normal and chlorinated wool) reveals that Group I - the non-contrast producing group - contains dyes with only one sulphonic group per molecule. Group II, intermediate in degree of contrast production between monosulphonated and disulphonated dyes, contains mostly dyestuffs which have one sulphonic group and one carboxyl group, or triphenylmethane dyes in which one sulphonic group is partly occupied in salt linkage with the amino-group. Dyes which contain two sulphonic groups make up group III. Group IV dyes, the ones which give the highest degree of contrast, have more than two sulphonic acid groups.

Vickerstaff (15) states that in general polysulphonated dyes are adsorbed to a much lower extent by wool from neutral solution than are monosulphonated dyes, but among the latter a great individuality of behavior is observed which substantiates the view that the presence or absence of hydrogen-bond-forming groups is important for neutral dyeing.

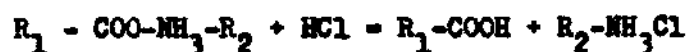
Dye-Fibre Binding Forces.--The phenomenon of the combination of dyes with fibres is known as adsorption. The adsorption forces which may hold a dye molecule at the surface of a fibre molecule are various and can be classified as follows (16):

1. Electrostatic attraction between charged sites in the substrate and ionic substances
2. Attraction by induction between ionic substances and a non-conducting substrate
3. Polar van der Waals' forces (e.g. hydrogen bonds)
4. Non-polar van der Waals' forces
5. Chemical forces

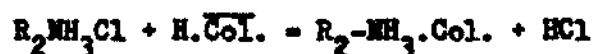
Derbyshire and Peters (17) state that the last type of adsorption force listed above (chemical forces) is of the covalent bond type and that these chemical forces occur in the dyeing of protein and polysaccharide fibres with acid dyes where the hydrogen ion is combined with the ionized carboxyl groups in the substrate.

Dyeing Wool with Acid Dyes.--Speakman (18) has shown that hot water is able to increase the size of the intermicellar spaces in wool and open up the structure of the micelles themselves. Because the latter consist

of long peptide chains, bridged across by linkages of the ammonium salt type, the process of micelle subdivision is greatly accentuated by acid and alkali. In acid solution in particular, the salt linkages are broken and the chains separated by a reaction of the following type:



In presence of color-acid, double decomposition then follows:



According to Elod (19), the reaction involved in dyeing wool with acid dyes may be summarized as follows:

1. Adsorption of the dyestuff anion on to the fibre surface
2. Diffusion of the anion through the cortical layer
3. Chemical reactions within the wool fibre (salt formation and other types of combination)

Effect of pH in Wool Dyeing.--The art of the dyer and the skill of the scientist have resulted in a very large number of dyeing processes. In some of these, hydrogen ion concentration plays little part; in others its role has yet to be fully investigated. More consideration of the pH factor tends the dyeing of wool fibres than other (non-protein) fibres since the former are amphoteric polypeptides.

With the acid type of dye for wool, the dyeing mechanism is believed to be the formation of a salt link between the sulphonic acid solubilizing groups in the dye molecule and the charged amino groups in the wool fibre. At pH's around the isoelectric point of the wool the maximum number of

internal salt links exist between carboxy and amino groups in the keratin. At lower pH's (greater hydrogen ion concentrations) the internal salt links are broken and unionised carboxyl (COOH) and positively charged amino (NH_3^+) groups are present. In the dyebath these latter groups form salt links with either dye anion or inorganic anions, usually sulphate ions. Combination occurs most rapidly with the small, mobile sulphate anions and these are then displaced from the amino sites by the larger and more slowly moving dye anion, with their greater affinity due to their ability to form subsidiary links (e.g. hydrogen bonds, van der Waals' attractions and the like) (20).

The number of available NH_3^+ groups is a function of the pH and hence the quantity of anion absorbed is also a function of the pH, the limit being reached when all the available primary amino groups are occupied by anions. Ender and Mueller (21) in their titration curves for wool, have shown the effect of pH when using Orange GG, Orange II and Wool Yellow (levelling, milling, and super milling dyes respectively). The shift of the curves to higher pH values, from Orange GG through Orange II to Wool Yellow is accompanied by an increase in wet fastness properties, and is believed due to the increased affinity of the anion. This is shown also for Napthalene Orange G and Coomassie Red G, typical acid levelling and acid milling dyes respectively.

Vickerstaff (22) points out the need for different dyeing methods for applying levelling and milling types of dyes since each dye has a critical pH above which little adsorption takes place. The pH must be brought below this critical figure for dyeing to occur, and a lower pH is required for the acid levelling dyes than for the acid milling dyes.

Further decrease of pH below the point at which an economic usage of dye is obtained reduces the concentration of dye in the bath to a very low value and this greatly reduces the migration and levelling properties of the system. Decreasing the pH also increases the rate of dyeing which may of itself lead to unlevelness. There is thus an optimum pH range for each dye in which good exhaustion is combined with adequate levelling, and this range occurs at higher pH values with dyes of higher affinity.

Wool Reserve Agents.--New methods for treating wool, and variations in the existing resist process techniques have resulted in a more extensive utilisation of wool reserve agents in the dyeing operation.

Elliott and Speakman (23) have shown the importance, in a resist treatment, of introducing new acidic groups by using reserve agents, in order to confer a negative potential on the fibre and, consequently, to decrease its attraction for acid dye molecules. The reserve agents used in their work were selected from synthetic tanning materials of the sulphonic acid type (e.g. Lissatan AC - a condensation product of a naphthalene sulphonic acid with formaldehyde, or Tanninol WR - a complex phenol-sulphur condensate oxidised in air).

Townend (24) has stated that many of the reserve agents (e.g. Lissatan AC and Tanninol WR) can be regarded as colorless dyes. Vickerstaff (25) concludes after studying Townend's results, (which show that dyes of slow dyeing characteristics appear best for the production of contrast) that the effects of reserve agents depend upon certain kinetic factors.

Very little information has appeared in the literature regarding wool reserve agents. This can be understood when consideration is given the original use of these products. They were developed for use as dispersing agents in vat dyeing, and as synthetic tanning products in the leather industry.

Effect of Temperature in Wool Dyeing.--The effect of temperature in wool dyeing, though of obvious importance, has received little attention, and this is especially true when this effect is considered in connection with other variables in the dyeing operation (e.g. dyestuff concentration, time of dyeing, and types of assistants used).

Steinhardt, Fugitt, and Harris (26) have made a study of the effect of temperature, on the process of combination with acids and bases, as regards the titration curve of wool. With increasing temperature the acid adsorption changes greatly. There is a marked decrease in the alkali combining capacity of wool at elevated temperatures.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

The following is a complete list of the machines and instruments utilized in conducting this investigation.

Atlas Fade-Ometer

Brown and Sharpe Yarn Reel

Christian-Becker Chainomatic Analytical Balance

J-2 Scott Vertical Tester (2 inch jaws)

Beckman pH Meter

Galvanized Steel Hot Water Bath

150 ml. Erlenmeyer Flasks (tests at 160° F and at the boil)

150 ml. Beakers (tests at 70° F)

CHAPTER IV

EXPERIMENTAL PROCEDURE

Preliminary Tests and Preparation for Dyeing

As a preliminary to dyeing, information was obtained regarding the yarn number, run, and cut; and twist per inch of the yarn. These tests were conducted under standard conditions (65 percent relative humidity and 70° F). The yarn was stored in the laboratory for a minimum of twenty-four hours in order that standard conditioning would be attained.

Determining the Yarn Number, Run, and Cut

The yarn number, run, and cut were determined by reeling 120-yard samples and weighing the samples on the Christian-Becker Chainomatic Balance. The length and weights were put in the following formula to determine the yarn number.

$$\text{Yarn Number} = \frac{\text{Length in Yards}}{\text{Weight in Grams}} \times \frac{7000}{840}$$

Five samples were taken from each of two cones and the average yarn number, obtained from the ten samples, was used in this experiment. The cut, and run of the yarn were determined by the following formulae:

$$\text{Cut} = \frac{500}{840} \times (\text{yarn number})$$

$$\text{Run} = \frac{1600}{840} \times (\text{yarn number})$$

The results are shown in Table 1 of the Appendix.

Twists Per Inch

The untwist-twist method was used to determine the twist per inch of the yarn. A ten-inch sample was inserted in the jaws of the Good-brand Twist Counter. The tension on the yarn was applied so that the indicator was at the top position. As the untwisting continued, a point was reached such that all the twist had been removed, and continued turning of the jaws at one end tended to insert twist in the yarn again to the extent that the yarn contracted and raised the indicator to its original position. Since the reading on the scale indicates the total turns required to remove all the twist in a ten inch sample, the reading obtained is divided by two and the resulting figure divided by ten to obtain the number of turns per inch. Five samples were taken from each of two cones of yarn. The average of the ten twist tests was taken as the twist per inch of the yarn. The results are shown in Table 2 in the Appendix.

Dyeing the Samples

Characteristics of the Dyes Used

The dyes used in this experiment, together with certain characteristics specified in the Colour Index, or determined by the writer are presented in Table 3 in the Appendix.

A series of dyeings was made to ascertain the maximum pH of dyeing of the several dyes (Table 3). Dyebaths, containing 4.0 percent dyestuff based on the weight of the fibres (owf), (using a 60-1 liquor

ratio), were prepared in the pH range 2.0 - 8.0 using diammonium phosphate or acetic acid. The dyeings were made in 150 ml. stoppered flasks at a temperature of 160° F for 1.0 hour.

Pretreatment of the Samples

The 0.5 gram samples of woollen yarn used in the dyeing experiments were pre-treated by one of the following two methods:

Method 1. Four 0.5 gram samples were immersed in a 200 cc. solution of 4.0 percent phenol which contained 10.0 percent (0.2 gram) of Synthraton ACA (owf) and treated for 1.0 hour at the boil. The samples were then removed from the bath, rinsed well in running water at room temperature, squeezed, and placed in the atmosphere to dry.

Method 2. A second group of four samples was pre-treated by immersing in a 200 cc. solution of 6.0 percent phosphoric acid which contained 10.0 percent of Synthraton ACA (owf), and treated for 1.0 hour at the boil. The samples were then removed from the bath, rinsed well and dried as in Method 1.

The Methods (1 and 2) of pretreatment were selected for best color contrast after several experiments with several acids at various concentrations and at different temperatures. All experiments were run for 1.0 hour. The conditions under which these preliminary experiments were run are summarized in the Table below.

Applications of Synthraton ACA in 10.0 and 20.0 percent concentrations (owf), at room temperature and at the boil indicated that concentrations in excess of 10.0 percent showed no improvement in

Acid	Conc. of Acid Solution	Temperature of Application	Temperature (°F) of Drying	Remarks
Acetic	5.0%	room	room	---
Acetic	5.0%	boil	room	---
Phenol	5.0%	room	room	---
Phenol	5.0%	boil	room	---
Phenol	10.0%	room	room	Visible Degradation
Phenol	10.0%	boil	room	Visible Degradation
Phosphoric	5.0%	room	130	---
Phosphoric	10.0%	room	130	---
Phosphoric	30.0%	room	130	Visible Degradation
Phosphoric	5.0%	boil	room	---
Phosphoric	10.0%	boil	room	---
Phosphoric	20.0%	boil	room	Visible Degradation
p-nitrophenol	2.0%	room	room	Visible Degradation
p-nitrophenol	2.0%	boil	room	Visible Degradation

results. However, it was necessary to apply this agent at the boil to achieve the desired results.

Experimental Dyeings

Many experiments were performed to determine the effect of various combinations and concentrations of dyes, effect of temperature and time,

and the effect of salt additions. After performing these experiments it was possible to devise a preferred method of producing two-color and two-tone effects on wool.

All experimental dyeings were performed with 0.5 gram samples of woolen yarn, the physical characteristics of which are given in Tables 1 and 2 in the Appendix. The liquor to yarn ratio for all dyeings was 60:1; the dyeings were agitated by hand with glass stirring rods. The experiments at 160° F were carried out in a constant temperature bath, the temperature of which was controlled to within $\pm 2.0^\circ$ F.

When the acid-treated fibres were placed in the dyebaths the baths became quite acidic. Before performing each dyeing with the pretreated material, the amount of the appropriate buffer solution necessary to bring the pH up to 6 was determined. This quantity of buffer solution was added to each bath before the samples were entered.

The salt used in each experiment was Glauber's Salt.

The following summary of experiments gives the preferred method for obtaining these results and the preliminary experiments (number III through VIII) which lead to the development of these preferred methods. In each preliminary experiment six different dyebaths were used.

Experiment I--Preferred Method for Obtaining Two-Color Effect

Two 0.5 gram samples of woolen yarn (one treated by Method 1, and the other treated by Method 2) were dyed in a dyebath, at a pH of 6, containing 2.0 percent (w/v) Alizarin Sapphire PS (G.I. 105) - an acid dye normally applied from a strongly acid dyebath - i.e., a level

dyeing dye) and 6.0 percent Fast Acid Yellow GS (C. I. 145 - an acid dye normally applied from a neutral or weakly acid dyebath - i.e., a supermilling dye). Dyeings were made for 1.0 hour at the boil. After the samples were removed from the dyebath they rinsed well in running water at about 160° F, and air dried.

Experiment II--Preferred Method for Obtaining a Two-Tone Effect

Two 0.5 gram samples of wool (one treated by Method 1, and the other treated by Method 2) were dyed, at a pH of 6, in a dyebath containing 2.0 percent (owf) Brilliant Scarlet 3R (C. I. 185 - an acid dye normally applied from a strongly acid dyebath) and Fast Acid Yellow GS (C. I. 145 - an acid dye normally applied from a neutral or weakly acid dyebath). Dyeings were made for 1.0 hour at the boil. After the samples were removed from the dyebath they were handled as in Experiment I.

Experiment III -- The Effect of Phenol

Dyes Used--

Dyebath 1. Alizarine Sapphire SESN (C. I. 1053 - an anthraquinone, monosulphonated, level dyeing dye)

Fast Acid Yellow GS (C. I. 145 - a monoazo, monosulphonated, supermilling dye)

Dyebath 2. Alizarine Sapphire FS (C. I. 1054 - an anthraquinone, disulphonated dye) Fast Acid Yellow GS (C. I. 145 - a monoazo, monosulphonated dye)

- Dyebath 3. Azo Rubine Extra (C. I. 179 - a monoazo, disulphonated dye) Fast Acid Yellow GS (C. I. 145 - a monoazo, monosulphonated dye)
- Dyebath 4. Acid Brilliant Red 4BL (C. I. 32 - a monoazo, trisulphonated dye) Fast Acid Yellow GS (C. I. 145 - a monoazo, monosulphonated dye)
- Dyebath 5. Fast Red S. Concentrated (C. I. 176 - a monoazo, monosulphonated dye) Fast Acid Yellow GS (C. I. 145 - a monoazo, monosulphonated dye)
- Dyebath 6. Brilliant Scarlet 3R (C. I. 185 - a monoazo, trisulphonated dye) Fast Acid Yellow GS (C. I. 145 - a monoazo, monosulphonated dye)

Pretreatment of Samples.--The samples were pretreated by Method 1, except the Synthraton ACA was omitted.

Time and Temperature.--The samples, one treated and one untreated, were entered into the dyebath at 160° F. The bath was heated to the boil during 20 minutes, and dyeing was continued at that temperature for one hour.

Salt.--15 percent (0.15 grams) (owf).

Dye Concentrations.--2.0 percent (owf) of each dye.

Experiment IV -- The Effect of Phosphoric Acid

Dyes Used.--Same as in Experiment III.

Pretreatment of Samples.--The samples were treated by Method 2, except the addition of Synthraton ACA was omitted.

Time and Temperature.--Same as in Experiment III.

Salt.--Same as in Experiment III.

Dye Concentrations.--Same as in Experiment III.

Experiment V -- The Effect of Synthraton ACA

Dyes Used.--Same as in Experiment III.

Pretreatment of Samples.--The samples were treated by Method 1, except there was no phenol present in the bath.

Time and Temperature.--Same as in Experiment III.

Salt.--Same as in Experiment III.

Experiment VI -- The Effect of Time and Temperature

Pretreatment of Samples.--One-half of the samples were treated by Method 1, and the other half by Method 2. Each dyebath contained a sample treated by Method 1, and also one treated by Method 2.

Time and Temperature.--The dyeings were made for 1.0 hour at 70° F, and then removed for observation. They were then re-entered into the same dyebath and the dyeings were continued for an additional hour at 160° F. After removing the samples for observation this procedure was again repeated at the boil.

Salt.--Same as in Experiment III.

Dye Concentrations.--Same as in Experiment III.

Experiment VII -- The Effect of Dyeing without Salt

Dyes Used.--Same as in Experiment III.

Pretreatment of Samples.--Same as in Experiment VI.

Salt.--No salt addition was made.

Dye Concentrations.--Same as in Experiment III.

Time and Temperature.--Same as in Experiment VI.

Experiment VIII -- The Effect of Dye Concentrations

Dyes Used.--Same as in Experiment III.

Pretreatment of Samples.--Same as in Experiment VI.

Time and Temperature.--Same as in Experiment VI.

Salt.--No salt addition was made.

Dye Concentrations.--Dyeings were made using 2.0 percent (owf) of the level dyeing dyes and 6.0 percent (owf) of the supermilling dyes in each dyebath. The concentrations were then reversed, (e. g., 6.0 percent of the level dyeing dyes and 2.0 percent of the supermilling dyes were placed in each dyebath).

Lightfastness Tests on Dyed Samples of Treated and Untreated Wool

Lightfastness tests on the three dyes used in Experiments I and II, when applied in the usual manner, as well as on dyeings made by the preferred methods described in Experiments I and II were performed by the Standard A. A. T. C. G. Method (182-2h).

Microscopic Examination

Fibres from the dyed yarns (Experiments I and II) were examined under a microscope both in cross-section and longitudinally in an effort to determine whether or not good penetration and even dyeing had been effected.

Effect of Pretreatment and Dyeing on Breaking Strength

50.0 gram samples of a woolen blanket, furnished by the Peerless Woolen Mills, were used for breaking strength evaluation. Dyeings were made as in Experiments I and II.

The results were tabulated, and the percent loss in breaking strength was calculated. See Tables 5-9 in the Appendix.

CHAPTER V

DISCUSSION OF RESULTS

A full explanation of the facts relating to the dyeing of wool with acid dyes of various chemical constitution has yet to appear in the literature. This lack of knowledge adds to the problem of discussing the results of treating wool with phosphoric acid, phenol, and Synthraton ACA and then dyeing with certain of these acid dyes. However, certain reasonable postulates can be offered in view of this work and previous work.

The Effect of Phenol, Phosphoric Acid and Synthraton ACA on Wool Dyeing.--

Samples pretreated with either phenol (Experiment III), or phosphoric acid (Experiment IV), when dyed in a dyebath containing two dyes, at a pH of 6, took up more of both dyestuffs than an untreated sample dyed in the same dyebath. For example, in Dyebath Number 1 both samples were dyed green but the treated sample was dyed darker. The sample, treated with Synthraton ACA, however, appeared to have picked up more of the supermilling dye.

This can be explained briefly by reference to the mechanism of wool dyeing which postulated that protons from the acids become attached to the COO^- groups of the fibre, whereas the anions of the acids occupy sites near the positively charged basic (NH_3^+) groups of the protein. The dye anions have a greater affinity for these sites than the acid

anions and consequently they displace the latter. The relative affinities of the dye anions would then determine any shade differences. (See General Discussion below)

The Effect of Phenol and Synthraton ACA on Wool.--Samples treated with phenol and Synthraton ACA (Method 1) dye darker shades than untreated samples dyed in the same dyebath containing two different dyestuffs. Referring again to Dyebath 1, the samples treated by Method 1 came out a much darker shade of green than did the untreated samples.

A possible explanation of this result might involve the fact that phenol is a relatively weak acid (K_a at 25° C is equal to 1.3×10^{-10}) and is not readily displaced from the wool fibre. This limits the action of Synthraton ACA in occupying many of the available dye sites, but does not suppress it completely. The level dyeing dye which is best applied under acid conditions, and the supermilling dye, which has a greater affinity for the fibre than does the Synthraton ACA and consequently displaces it, are therefore able to dye the sample more completely.

The Effect of Phosphoric Acid and Synthraton ACA.--A wool sample treated with phosphoric acid and Synthraton ACA, when dyed in a dyebath containing a supermilling dye and a level dyeing dye, adsorbed the supermilling dye in the normal manner whereas the adsorption of the level dyeing dye was practically negligible. With reference to the dyes in Dyebath 1, the treated sample adsorbed only the yellow dye whereas the untreated sample adsorbed both the yellow and blue dye.

This phenomenon can be explained by considering the strength of the acid and the relative affinities of the dyes and Synthraton ACA.

When wool is treated with phosphoric acid (K_a at 25° C is equal to 7.5×10^{-3}) and Synthraton ACA, the acid fills the available sites rapidly but is then readily displaced by the Synthraton ACA, leaving essentially all the dye sites occupied by the latter. The level dyeing dye, having less affinity for wool than Synthraton ACA, cannot displace it and will not dye the treated material in the normal manner. Another possible explanation is that phosphoric acid, being a stronger acid than phenol, is removed more rapidly from the wool to the dye bath. This causes an increase in the pH of the wool so that the fiber is unable to adsorb the level dyeing dye.

General Discussion

The Affinity of Wool for Acids.—The pH at the midpoint of the titration curve of wool gives an indication of the approximate affinity of acids for wool, and may be applied to any available titration curves. This raises the question as to what is the maximum acid binding power of wool. Earlier workers (27), (28), (29), (30) have used values of 0.80-0.85 equivalent of acid per kilogram of wool apparently as determined by inspection of the titration curve. From the results of the titration curves of the acids used (19 different acids) attempts have been made to correlate the molecular weight, shape of anions and strength of acid with their affinity. There is a clear tendency for the affinity to increase with increasing molecular weight or introduction of polar groups, the behavior which may be expected if the affinity arises from Van der Waals forces between the dye and the fibres. The change in affinity on introduction of any group is roughly additive. Anions which are

planar generally have a greater affinity for wool than compact three-dimensional ions or chain-like ions of the same weight.

The Effect of Mono- and Polysulphonated Dyes and Synthraton ACA.--

Vickerstaff (31) states that for a monosulphonated dye, each basic group in the fibre can accommodate one dye molecule, and it may well be that in a commercial dyeing of 1 to 3 percent of standard dye that the whole of the dye can be accommodated in the outer layer of the wool fibres, so that little diffusion in the fibre need take place before the dyebath is exhausted. Mechanical factors will then determine the rate of dyeing. With a trisulphonated dye, however, the same outer layer of the fibre can take up only one-third as many molecules of dye, and supposing the dyebaths to be equimolecular, it may then be necessary for diffusion in the fibre to take place before the dyebath becomes exhausted. Here, mechanical factors are less important since the rate of dyeing will depend more in the rate of diffusion inside the fibre.

By Adding a Resist Agent (Colorless Dye).--When some of the dye sites are taken up the necessity for diffusion of the trisulphonated dye into the fibre is emphasized.

Other factors also are important, as for example the varying affinities of the monosulphonated and polysulphonated dyes. From the standpoint of relative affinities it is necessary to point out that monosulphonated dyes have a far greater affinity for wool than do polysulphonates. This affinity difference is so pronounced that monosulphonated dyes must be applied from nearly neutral baths in order to control their initial strike action and so eliminate streaky dyeings.

Insufficient data prevents an adequate explanation of the exact reactions taking place in all these treatments, but a consideration of the mechanical and affinity factors mentioned above allows a fairly reasonable explanation for the results observed.

Effect of Time, Temperature, Salt and Dyestuff Concentration on Wool

Dyeing.--An increase in both dyeing time and temperature produced greater dyebath exhaustion and consequently darker shades. Contrast effects were not as distinct when longer dyeing times and higher dyeing temperatures were used. Best results were obtained by dyeing the samples for one hour at the boil. Dyebath exhaustion was very poor for dyeings made for one hour at 70° F, and improved only slightly when dyeing time was increased to two hours. For dyeings made for one hour at 160° F and 212° F the dyebath exhaustion was improved appreciably, at the higher temperature; but when dyeing time was increased to two hours the contrast produced was not as great.

Dyeing without salt (Experiment VII) reduced dyebath exhaustion; the samples were not dyed as deeply as those obtained from a dyebath containing salt.

Varying the dyestuff concentrations of the dyestuff combinations (Experiment VIII) showed that better contrasts are produced when the dyebath contained a higher percentage of the supermilling dye than of the level dyeing dye. Using equal concentrations of the dyestuffs produced a contrast that was inferior to contrasts produced using higher concentrations of the supermilling dye. When the concentrations were

reversed (i.e., a higher percentage of the level dyeing dye was used) the contrast effect produced was less satisfactory.

Lightfastness Tests.--An examination of the samples after exposures in the Atlas Fadeometer indicated that neither the methods of pretreatment nor the dyeing procedure altered the lightfastness properties obtained by regular dyeing procedures.

Microscopic Examinations.--Fibres pulled from the dyed yarn samples and examined longitudinally under a microscope showed an uneven penetration of the two dyes into the fibre. It is believed, however, that this defect would be alleviated in the normal finishing operations. However, when examined without the use of a microscope the samples appeared to be dyed fairly uniformly.

Cross-sections of the fibres showed that very good penetration of the dyestuffs had been obtained. Samples that had taken up both dyes showed color interspersed throughout the sample.

Breaking Strength Tests.--The average breaking strength of the samples dyed under ordinary conditions was 175 pounds for warp breaks and 160 pounds for filling breaks.

For samples treated by Method 1, and dyed as in Experiment I, the average loss in breaking strength was found to be 16 percent for warp breaks and 20 percent for filling breaks. For samples treated by Method 2, and dyed as in Experiment 1, the breaking strength loss was negligible. Similar results were obtained for loss in breaking strengths when dyeings were made as in Experiment II.

See Tables 3-9 for details of the breaking strength tests.

CHAPTER VI

CONCLUSIONS

It can be concluded that a new and satisfactory method for producing two-color and two-tone effects on woolen fabrics has been developed. This was accomplished by the discovery of suitable pre-treatment methods; by employing suitable combinations of dyestuffs having the desired dyeing characteristics and chemical constitution; and by carefully controlling the dyeing operation.

It has been established that a pretreatment of woolen fabrics using phenol and Synthraton ACA causes the treated material to take up more of a levelling dye, whereas a sample treated with phosphoric acid and Synthraton ACA results in a reduction of the amount of a levelling dye taken up.

The evidence obtained from the experiments performed indicates that selection of dyestuffs having the desired chemical constitution is essential, and determines to a large measure the quality of the contrast produced. Also, the time of dyeing, addition of salt and temperature of dyeing affect the contrast produced.

It should be clearly understood that the solution of the problem of determining the effect of each factor separately or the interrelationships which exists between the factors has not been fully explained. Hence these conclusions are of necessity tentative until further evidence can be obtained.

CHAPTER VII

RECOMMENDATIONS

Further investigation of methods for producing two-color and two-tone effects on wool by using phosphoric acid and phenol, together with wool reserve agents is strongly recommended. Particular attention should be given the effect of using level dyeing dyes and supermilling dyes from various chemical classes, e.g., anthraquinone as well as azo dyestuffs.

An extensive examination should be made of the following factors, an understanding of which is considered to be essential before an explanation of the reactions of this process can be advanced:

1. Determination of the amount of Synthraton ACA taken up by wool when pretreated with phenol or phosphoric acid.
2. Determination of the amount of Synthraton ACA displaced by milling dyes.
3. Determination of the amount of phenol and phosphoric acid taken up by wool.
4. Determination of the change in concentration of Synthraton ACA during dyeing with a milling and level dyeing dyes.

After the above studies have been made, other acids having characteristics similar to phenol and phosphoric acid should be evaluated for use in this process, as well as with other wool reserve agents.

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APPENDIX

Table 1. Yarn Number, Run, and Cut of Undyed Woolen Yarn

Specimen Number	Weight of 120 Yards (Grains)	Yarn Number or Count
1	193.74	5.16
2	190.05	5.26
3	176.07	5.61
4	184.90	5.41
5	196.33	5.09
6	192.44	5.19
7	191.93	5.23
8	188.41	5.32
9	178.66	5.60
10	180.70	5.54
11	179.88	5.56
12	187.36	5.34
13	193.66	5.14
14	191.14	5.23
15	185.69	5.38
16	190.11	5.27
17	196.54	5.07
18	183.14	5.46
19	181.27	5.52
20	192.07	5.20
Total		106.59
Average		5.33
Cut	$\frac{560}{840} \times 5.33$	3.51
Run	$\frac{1600}{840} \times 5.33$	9.88

Table 2. Twists per Inch in Undyed Woolen Yarn

Specimen Number	Twists per Inch	Specimen Number	Twists per Inch
1	9.80	11	10.05
2	10.15	12	9.90
3	10.00	13	10.20
4	10.20	14	10.25
5	10.18	15	10.05
6	10.05	16	10.00
7	10.15	17	10.15
8	9.90	18	10.10
9	10.10	19	9.90
10	10.00	20	10.15
Total			200.75
Average			10.04

Table 3. Characteristics of Dyes Used

LEVEL DYES

Name and Colour Index No.	Class	Dyebath pH for 6.0% Solution of Dye
Acid Brilliant Red 4BL C. I. 32	Monoazo	6.8
Alizarine Sapphire SESW C. I. 1055	Anthraquinone	3.2
Alizarine Sapphire FS C. I. 1054	Anthraquinone	9.2
Aso Rubine Extra C. I. 179	Monoazo	6.9
Brilliant Scarlet 3R C. I. 185	Monoazo	7.8
Fast Red B. Conc. C. I. 176	Monoazo	8.4
Fast Wool Yellow 3GL C. I. 636	Pyrazolone	7.2

MILLING AND SUPER MILLING

Fast Acid Yellow GS C. I. 145	Monoazo	6.8
Fast Wool Cyanone C. I. 289	Disazo	8.4
Milling Yellow NGS C. I. 138	Monoazo	7.2
Wool Fast Blue GL C. I. 833	Isobosindones	6.7

Table 3'. Characteristics of Dyes Used

LEVEL DYES

Name and Colour Index No.	No. of Sulphonic Groups	Maximum Dyeing pH
Acid Brilliant Red 4BL C. I. 32	3	--
Alizarine Sapphire SRSW C. I. 1055	1	6.0
Alizarine Sapphire FS C. I. 1054	2	--
Aso Rubine Extra C. I. 179	2	--
Brilliant Scarlet 3R C. I. 185	3	--
Fast Red S. Conc. C. I. 176	1	--
Fast Wool Yellow 3GL C. I. 636	1	--

MILLING AND SUPER MILLING DYES

Fast Acid Yellow A5 C. I. 145	1	--
Fast Wool Cyanone C. I. 289	1	--
Milling Yellow M08 C. I. 138	1	--
Wool Fast Blue GL C. I. 833	--	--

Table 4. Breaking Strength Determination of Undyed Woolen Fabric

Specimen Number	Breaking Strength (lbs)
	<u>WARP</u>
1	160.0
2	180.0
3	175.0
4	170.0
5	170.0
6	180.0
7	175.0
8	180.0
9	185.0
10	180.0
Total	1755.0
Average	175.5

Table 5. Breaking Strength Determination of Undyed Woolen Fabric

Specimen Number	Breaking Strength (lbs)
<u>FILLING</u>	
1	155.0
2	165.0
3	165.0
4	160.0
5	150.0
6	165.0
7	160.0
8	165.0
9	160.0
10	155.0
Total	1600.0
Average	160.0

Table 6. Degradation of Wool by Phenol and Synthraton ACA when Dyed with Milling Yellow NGS (6.0 percent) and Alizarine Sapphire FS (2.0 percent)

Specimen Number	Breaking Strength (Pounds)	Loss in Breaking Strength (%)
	<u>WARP</u>	
1	140.0	15.15
2	140.0	15.15
3	145.0	12.12
4	137.0	16.96
5	135.0	18.19
6	135.0	18.19
7	130.0	21.20
8	140.0	15.15
9	145.0	12.12
10	130.0	21.20
Total		163.43
Average		16.34

Table 7. Degradation of Wool by Phenol and Synthran ACA when Dyed with Milling Yellow NGS (6.0 percent) and Alisarine Sapphire FS (2.0 percent)

Specimen Number	Breaking Strength (Pounds)	Loss in Breaking Strength (%)
	<u>FILLING</u>	
1	125.0	21.92
2	130.0	18.65
3	135.0	15.61
4	127.0	20.25
5	125.0	21.92
6	130.0	18.65
7	132.0	17.50
8	122.0	23.10
9	125.0	21.92
10	130.0	18.65
Total		198.17
Average		19.82

Table 8. Degradation of Wool by Phosphoric Acid and Synthraton ACA when Dyed with Milling Yellow NGS (6.0 percent) and Alizarine Sapphire FS (2.0 percent).

Specimen Number	Breaking Strength (Pounds)	Loss in Breaking Strength (%)
	<u>WARP</u>	
1	180.0	--
2	170.0	--
3	165.0	--
4	165.0	--
5	170.0	--
6	170.0	--
7	175.0	--
8	165.0	--
9	170.0	--
10	175.0	--

Note: Loss in breaking strength was negligible

Table 9. Degradation of Wool by Phosphoric Acid and Synthrasan ACA when Dyed with Milling Yellow NGS (6.0 percent) and Alizarine Sapphire FS (2.0 percent).

Specimen Number	Breaking Strength (Pounds)	Loss in Breaking Strength (%)
	<u>FILLING</u>	
1	155.0	--
2	160.0	--
3	158.0	--
4	165.0	--
5	160.0	--
6	155.0	--
7	160.0	--
8	150.0	--
9	155.0	--
10	157.0	--

Note: Loss in breaking strength was negligible