# United States Patent [19]

**Shibukawa et al.**

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[54] **BLENDING NEUTRAL DYEING 1:2 PREMETALLIZED AZO DYED ACID MODIFIED ACRYLIC FIBER WITH THE SAME FIBER UNDYED AND DISPERSE OR CATIONIC DYEING THE BLEND**


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[21] Appl. No.: **259,840**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 654,054, July 18, 1967, abandoned.

[52] **U.S. Cl.** ..... **8/21 A,** 8/168, 8/42 A, 8/26, 8/15

[51] **Int. Cl.** ..... **D06p 3/82**

[58] **Field of Search** ..... 8/15, 21 A, 168, 65, 42 A



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[57] **ABSTRACT**

An acrylic fiber containing acid groups but no basic groups is dyed with a neutral dyeing 1:2 type premetallized acid dye in a bath containing at least one water-soluble inorganic monovalent metal salt, divalent metal salt or ammonium salt. The resultant dyed material is deeply colored and of excellent fastness, is characterized by minimum dye migration, and is therefore useful in the manufacture of multi-colored dyed acrylic fiber materials.


**2 Claims, No Drawings**

# BLENDING NEUTRAL DYEING 1:2 PREMETALLIZED AZO DYED ACID MODIFIED ACRYLIC FIBER WITH THE SAME FIBER UNDYED AND DISPERSE OR CATIONIC DYEING THE BLEND

This application is a continuation-in-part of Ser. No. 654,054, filed July 18, 1967, now abandoned.

This invention relates to a method for multi-colored dyeing of acrylic textile materials. More particularly, it relates to a method for multi-colored dyeing of textile material composed of fibers of acrylic polymer containing acid groups (hereinafter sometimes referred to as acrylic synthetic fiber containing no basic groups). In accordance with this method, a first dark-shade dyeing of a part of the fiber material is carried out with a neutral dyeing 1:2 type pre-metallized acid dye which possesses excellent potting fastness, and after the fiber material thus dyed is mix-spun or otherwise blended with the counterpart fiber material, cross dyeing of the resulting textile material is carried out with another dye of a different color.

With regard to cross dyeing, where a textile material composed of the same or two similar fibers having identical functional groups is dyed to a variegated color pattern, it has been conventional practice to carry out the first dyeing of that part of the textile material to be dyed in a dark shade, and then to carry out a second dyeing (cross dyeing) of the entire assembly with a dye whose color contrasts with that of the dye used in the first dyeing.

However, when a textile material composed of an acrylic fiber containing acidic groups but no basic groups which has been dyed to a dark shade with a dye exhibiting cationic behavior in the dyeing bath (hereinafter referred to as cationic dye) is mixed with an undyed textile material and the entire assembly is subjected to a second dyeing with another cationic dye of a different color to obtain a multi-colored dye article, the dye adsorbed on that part of the material which has been dyed in the first dyeing tends to bleed out during the second dyeing. The result is that the fiber to be dyed in the second dyeing is stained, and accordingly, the objective two color effect can not be obtained.

The acrylic textile materials which are subjected to dyeing in accordance with the present invention are composed of acrylic polymers containing acid groups but no basic groups. In the process of producing the acrylic polymer or copolymer, strong acidic groups such as sulfate or sulfonate groups are introduced into the terminals of the molecule through the utilization of persulfuric acid, sulfurous acid, bisulfuric acid or their salts as a polymerization initiator. Alternatively, the acidic groups are introduced through copolymerization with unsaturated monomers containing sulfonate groups, such as styrenesulfonic acid, vinyl sulfonic acid, allylsulfonic acid, methallylsulfonic acid, as well as their salts, or with unsaturated monomers containing carboxylic acid groups, such as acrylic acid, methacrylic acid and itaconic acid as well as their salts. By these methods the resultant acrylic fiber contains acid groups but no basic groups, and is thus rendered receptive to cationic dyes. Particularly preferred are those acrylic fibers containing sulfonate groups.

Cationic dyes are widely used as well as disperse dyes to dye hydrophobic synthetic fibers. The dyeing of an acrylic synthetic fiber with a cationic dye is apparently



based on the reversible ion-exchange reaction schematically illustrated below.

$$(\text{fiber}-)-SO_3^-Na^+ + (\text{dye})^+Cl^- \rightleftarrows (\text{fiber}-)-SO_3^-{}_{(dye)}^+ + {}_{Na}^+{}_{Cl}^-$$

It is apparent that if a large amount of the cationic substance to be adsorbed selectively on the acidic groups of the fiber is freshly added to the dyeing system, the reaction proceeds from right to left and, consequently, the dye which has already attached itself to the fiber is liberated as it undergoes an exchange with the freshly added cationic substance.

This phenomenon becomes a practical problem when there are introduced changes such as in pH, due to the addition of acid or alkali, or when other materials are added to the dye bath, such as the addition of inorganic salts, the cationic dye of a different color to be used in the cross or second dyeing bath, and the cationic retarder to be used in said second bath. The result is that the dark-shade dye used in the first bath bleeds out into the second bath, so that the fiber to be dyed in the second bath can not be dyed satisfactorily. This phenomonon is observed even when using the cationic dyes described in the Japanese Industrial Standards (JIS) as being satisfactory in potting fastness. Thus, such a dyeing process can not be successfully adopted for practical purposes.

As regards disperse dyes, it is known from the Journal of the Society of Fiber Science and Technology, Japan, Vol. 21, (March, 1965) pp. 156 to 163 and the synopsis of the proceedings of the Spring Convention of the Society of Fiber Science and and Technology, Japan (1964), pp. 28 that the dyeing mechanism is based on Henry's distribution law. From this fact, as well as from the fact that the diffusion of dye into a fiber is considerably increased above 80° C., the disperse dye which has once been adsorbed on the textile substrate is redistributed into the undyed substrate fiber through the second dyeing bath.

The conclusion that may be drawn from the above observations is that such dyeing processes can not be practically applied.

It has now been discovered that when an acrylic synthetic fiber containing acid groups but containing no basic groups is dyed with neutral dyeing 1:2 type premetallized acid dyes in a bath containing at least one water-soluble inorganic salt selected from the group consisting of monovalent metal salts, divalent metal salts and ammonium salts, a dyed material which is deeply colored and possesses excellent fastness, with a minimum of dye migration in particular, is obtained. The present invention is based on this novel finding.

The principal object of the invention is to obtain an unstained multi-colored dyed material of an acrylic synthetic fiber containing strong acidic dissociable groups but no basic dissociable groups. Another object is to attain a multi-colored acrylic textile product which has excellent fastness. Other objects will become apparent from the following description of the invention.

The objects of the invention can be accomplished by carrying out a first dyeing of an acrylic textile material in a dark shade with a neutral dyeing 1:2 type premetallized acid dye in the presence of at least one water-soluble inorganic salt selected from the group consisting of monovalent metal salts, divalent metal salts and ammonium salts.

The textile material is selected from fibers, spun yarns and other textile products, whether woven or knitted, composed only of acrylic synthetic fibers containing acid groups but no basic groups.

Then, a second dyeing of the other textile material is carried out with a cationic or disperse dye of a different color after the first-mentioned dyed material is combined with the second mentioned undyed material by means of blending, mixspinning, mix-plying, blend-weaving or knitting. Thus, the second-mentioned material would not be dyed in the first dyeing, but only in the second dyeing.

As to the dyeing of the acrylic synthetic fiber containing acid groups but no basic groups, with a neutral dyeing 1:2 1type pre-metallized acid dye, kinetic and equilibrium studies of such dyeing behavior have been carefully investigated. It has been discovered that while the diffusion of both cationic and disperse dyes increases greatly as the dye bath temperature reaches 70° C to 90° C, the diffusion of the neutral dyeing 1:2 type pre-metallized acid dyes at these temperatures is low due to their large molecular volume, and that as the dye bath temperature is increased to more than 100° C to 110° C, the microbrownian motion of the fiber molecules is so invigorated that the diffusion of the pre-metallized dyes into the fiber is conspicuously increased, resulting in an adsorption isotherm which is substantially shown as Henry's distribution law. Furthermore, when the inorganic salt used in the present invention is added to the dye bath, the salt considerably increases the distribution of the 1:2 type pre-metallized acid dye into the fiber, thereby making it possible to obtain a dark shade, which has been considered particularly difficult to attain.

Generally speaking, dyeing to a dark shade an acrylic synthetic fiber containing acid groups but no basic groups with a neutral dyeing 1:2 type pre-metallized acid dye may be attained by dyeing the material in a dye bath containing at least 0.5 percent by weight of a divalent metal salt or at least 1.0 percent by weight of a monovalent metal or ammonium salt, based on the weight of the dye bath, at a dyeing temperature of 100° C or higher. Stated differently, it requires the use of temperatures of at least 100° C., preferably 100°–130° C., to effect a good diffusion of the dyestuff, which possesses a large molecular volume, into the fiber, and any dye bath temperature below 100° C. would result in a considerable reduction in the dyeability of the fiber. A temperature above 130° C is not preferable because the acrylic fiber will be deteriorated at such a high temperature.

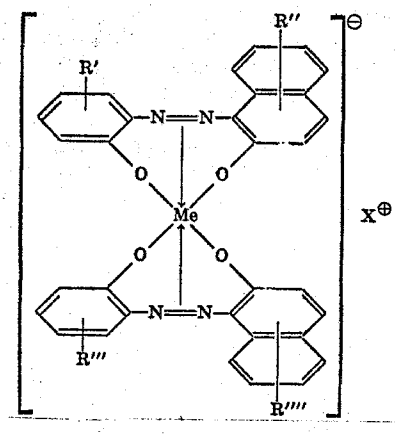
The addition of an inorganic salt to the dyeing bath is essential when an increased partition of the dye to the fiber is to be attained. Thus, the presence of 1.0 percent by weight or more of the monovalent metal or ammonium salts or 0.5 percent by weight or more of a divalent metal salt in the dye bath is essential, and no practically satisfactory dyeing can be expected when the concentration of the inorganic salt is lower than this amount. It is preferable that the amount of the inorganic salt(s) does not exceed 5 percent by weight because the presence of an excessive amount may cause undesirable aggregation of the dye.

The water-soluble inorganic monovalent metal and ammonium salts that can be effectively employed according to this invention include the halides, sulfates and phosphates or alkali metals (sodium, potassium, etc.) and ammonia, those salts which are neutral in aqueous solutions being particularly preferred. Specific examples of such salts are sodium sulfate, sodium chloride, ammonium chloride, ammonium sulfate and potassium sulfate. The salts may be effectively employed either singly or in combination with one or more others.

Examples of water-soluble inorganic divalent metal salts are calcium chloride, barium chloride, zinc chloride, magnesium chloride, cadmium chloride, zinc sulfate, magnesium sulfate, zinc nitrate, cadmium nitrate, calcium thiocyanate and mixtures of any two or more of them. A further advantage of the use of such divalent metal salt is that the divalent metal ion, e.g. $Ca^{++}$, $Ba^{++}$ and $Zn^{++}$, will combine with the acid groups in the fiber to block the sites for the cationic dye so that in the subsequent dyeing with a cationic dye the staining of the first-dyed fiber with the second dye (cationic dye) is prevented. Therefore the use of the divalent salts is preferred.

As will be seen from the previously mentioned fact that the dyeing behavior of the neutral dyeing 1:2 type premetallized acid dye relative to the acrylic synthetic fiber substantially follows Henry's distribution law, it is necessary, when the fiber is to be dyed to a dark shade, that the dye concentration of the bath is high. For this purpose, the initial concentration of the dye in the bath should be 0.2 percent by weight or more. For economical reasons, the upper limit of the dye concentration would be about 1 percent.

The neutral dyeing 1:2 type pre-metallized acid dyes used in this invention are those in which two dye-component molecules are coordinated on a single metal atom, as represented by the formula




wherein Me is chromium or cobalt R', R'', R''' and R'''' are, independently of each other, substituents ordinarily possessed by dyestuffs, such as sulfonyl, sulphamyl, lower(1–6) acylamino, lower (1–6) alkyl, phenyl, nitro and hydroxyl groups, and X is a monovalent metal atom, such as sodium. The structure of the dye so formed is anionic, with the counterpart ion being ex-

emplified by the sodium ion. All these dyes are water-soluble chromium- or cobalt-containing azo dyes containing no ionizing lyophilic groups and no ionizing polar groups, in which two dye molecules are combined with one metal atom. Thus, the dyes do not contain sulfonic acid groups. Any such neutral dyeing 1:2 premetallized acid dye can be used in the present invention, such as those fully described in The Journal of the Society of Dyers and Colourists, Vol. 71 (1955) pages 705-724. These neutral dyeing 1:2 type premetallized acid dyes are examplified by C.I. 11640, C.I. 11650, C.I. 11836, C.I. 11837, C.I. 12695, C.I. 12696, C.I. 12714, C.I. 15681, C.I. 15707, C.I. 15708, C.I. 15900, C.I. 13890, C.I. 17941, C.I. 18762, C.I. 18690, C.I. 20018, C.I. 12195, C.I. 15675 and C.I. 12197.

Generally, this first dyeing with 1:2 type premetallized acid dye is conducted at a liquor ratio of 1:8 to 1:50 for about 1–3 hours at a pH of from 5 to 9.

The thus dyed textile material is then combined with undyed textile material of the same or similar acrylic polymer containing acid groups but no basic groups, by means of, for example, staple-mixing, blending, mix-spinning, mix-twisting, mix-weaving, mix-knitting, etc. Thereafter the entire textile material is subjected to a second or cross-dyeing with a cationic optical brightener or a cationic or disperse dye of a color different from that of the 1:2 type pre-metallized acid dye. The second dyeing may be conducted in a conventional manner. Thus, for example, the second dyeing is conducted in a bath containing 0.1–3.0 percent (based on the weight of the textile material) of the dye at pH 3.5–7.0 with a liquor ratio of 1:30 to 1:100.

Examples of cationic dyes useful in the second dyeing are C.I. 42025, C.I. 51005, C.I. 51004, C.I. 42140, C.I. 48055, C.I. 48065, C.I. 48035, C.I. 48040, C.I. 48020, C.I. 48013, C.I. 48015 and C.I. 42040.

The textile material resulting from the second dyeing shows no signs of bleeding from the first-dyed fiber, that is, no staining of the second-dyed fiber. Thus, the resulting material shows an attractive two color effect.

The acrylic synthetic fiber containing acid groups but no basic groups which is employed according to this invention is an acrylic fiber of acrylonitrile polymer or an acrylonitrile copolymer (containing at least 80 percent by weight of acrylonitrile units) free from copolymeric components containing basic groups.

The abbreviation C.I. as used herein stands for Color Index, 2nd editions, 1956 and Supplement, 1963, published by the Society of Dyers and Colourists, Bradford, England and the American Association of Textile Chemists and Colourists, Lowell, Massachusetts, U.S.A.

Some typical embodiments of the present invention will be given hereinafter to further illustrate the invention. In the examples, all percentages and parts are by weight, unless otherwise specified. The symbol "o.w.f." means percent based on weight of the fiber.

## EXAMPLE 1

To 97.7 parts of a dyeing bath are added 0.4 part of 1:2 type pre-metallized acid dye, C.I. 15675 and 2.0 parts of sodium sulfate, and 10 parts of acrylic fiber A (a copolymer of 90 percent acrylonitrile and 10 percent methyl acrylate containing 20 millimoles of sulfonate groups per kg. of fiber) are dyed at a dyeing temperature of 120° C for 2 hours, at the end of which time the dyed fiber is taken out. After soaping, the dyed fiber is washed three times, each with 50 times as much water relative to the fiber. The fiber is oiled and then dried.

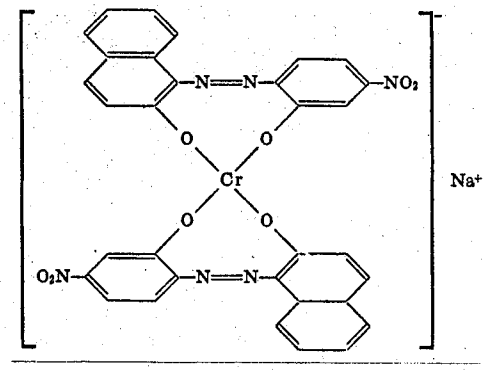
Then 20 parts of the above dyed fiber are mix-spun with 80 parts of undyed acrylic fiber A to make a "melange" yarn of white and reddish purple. Two parts of this yarn are dipped in 98 parts of a dye bath composed of 0.03 percent cationic dye C.I. 48035, 0.06 percent acetic acid, 0.1 percent sodium sulfate, 0.04 percent cationic retarder and 99.79 percent water, and is dyed as such at temperatures increasing by degrees from 60° C to about 100° C over a period of 60 minutes, followed by further dyeing at about 100° C for an additional 30 minutes.

The resulting variegated dyed yarn shows no signs of bleeding from the previously dyed fiber, that is, no staining of the second-dyed fiber, and the latter fiber thus assumes a bright orange shade. The result is an attractive "melange" yarn of orange and reddish purple.

On the other hand, a similar yarn composed of fibers one of which has been dyed with a first dyeing bath of cationic dye, C.I. 48020, and then after blending with the other fiber dyed to a different shade, shows extensive signs of staining of the second-dyed fiber owing to the bleeding-out of dye from the first-dyed fiber, with the total yarn assuming a brownish color. Thus, the expected effect of variegated dyeing is not observed with this yarn.

## EXAMPLE 2

Acrylic fiber B (a copolymer of 91 percent acrylonitrile, 8.8 percent methyl acrylate and 0.2 percent allyl sulfonic acid, containing 48 millimols of acid groups per kg. of fiber) is dyed by a package dyeing machine under the following conditions: 5 percent o.w.f. of 1:2 type pre-metallized acid dye of the formula

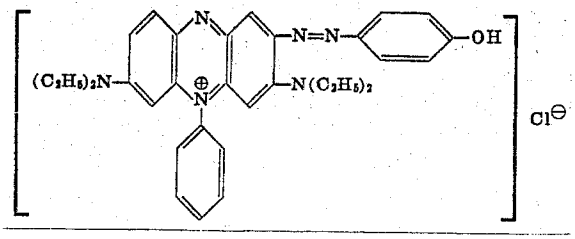



20 percent o.w.f. of sodium chloride, liquor ratio 1/20, dyeing temperature 120° C, 2 hours. The dyed fiber is taken out from the package dyer and is soaped with 0.5 g/l of a nonionic surface active agent (polyoxyethylene lauryl ether) at 60° C for 20 minutes, at the end of which time the fiber is washed three times, each time

with 50 times as much water relative to the fiber. The fiber is oiled and then dried.

Then 20 parts of the dyed fiber are mix-spun with 20 parts of undyed acrylic fiber B to prepare a "melange" yarn, which is dyed under the following conditions: 0.1 percent o.w.f. of cationic dye, C.I. 42025, 1 percent o.w.f. of acetic acid, 10 percent o.w.f. of sodium sulfate, 3 percent o.w.f. of cationic retarder, liquor ratio 1/50, with dyeing bath temperature increasing gradually from 60° C to about 100° C over a period of 1 hour, followed by further dyeing at about 100° C for an additional 30 minutes. The resulting yarn shows no sign of bleeding from the first-dyed fiber, with the cross dyed fiber assuming a brilliant pale bluish shade. Thus, a very satisfactory cross-dyed yarn is obtained.

On the other hand, a first fiber similar to the first one used above is dyed by a package dyeing machine under the following conditions: 5 percent o.w.f. cationic black dye of the formula



1 percent o.w.f. sodium acetate, liquor ratio 1/20, with the dyeing bath temperature increasing gradually from 60° C to about 100° C over a period of 40 minutes, followed by further dyeing at about 100° C for an additional 90 minutes, at the end of which time the dyed fiber is processed and blended with the second fiber in the same manner as above. The yarn so prepared is cross-dyed as above. The result is that the second-dyed fiber is extensively stained due to the bleeding out of the first dyed fiber, giving rise to a yarn of poor saleability.

## EXAMPLE 3

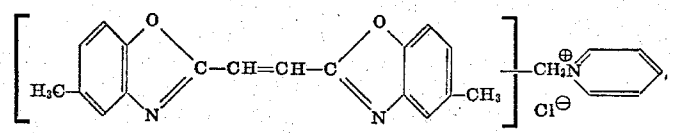
Acrylic fiber B is dyed with the 1:2 type pre-metalized acid dye and after-treated in the same manner as in Example 2. The fiber is then spun into yarn. One part of the dyed yarn is mix-twisted with 2 parts of yarn which is composed of undyed acrylic fiber B, and the resulting mix-twisted yarn is machine-knitted. The resulting knitted fabric is dyed under the following conditions: 0.5 percent o.w.f. cationic dye, C.I. 48055, 3 percent o.w.f. acetic acid, 1 percent o.w.f. sodium acetate, 2.9 percent o.w.f. cationic retarder, liquor ratio 1/20, with the dye bath temperature increasing gradually from 60° C to about 100° C over a period of 40 minutes, followed by further dyeing at about 100° C for an additional 45 minutes.

The resulting cross-dyed fabric has an attractively black-dotted pattern, showing no signs of bleeding of the first dye, that is, no staining of the second-dyed yarn.

On the other hand, when a first yarn dyed with the cationic black dye as in Example 2 is employed, the bleeding of dye from the first-dyed yarn results in extensive staining of the second-dyed yarn. The entire fabric assumes a grayish shade, and the desired effect of cross dyeing is completely absent.

## EXAMPLE 4

Acrylic fiber B is dyed by means of a package dyer under the following conditions: 8 percent o.w.f. 1:2 type pre-metallized acid dye used in Example 2, 20 percent o.w.f. potassium sulfate, liquor ratio 1/20, dyeing bath temperature 120° C, 2 hours. The dyed fiber is processed in the same manner as in Example 2 to prepare a colored yarn. 1 part of the dyed yarn is mix-twisted with 5 parts of yarn composed of undyed acrylic fiber B, and for the purpose of enhancing the whiteness of the undyed yarn, the mixed yarn is dyed under the following conditions: 0.8 percent o.w.f. cationic optional brightener of the formula



10 percent o.w.f. sodium sulfate, 1 percent o.w.f. acetic acid, liquor ratio 1/100, with the dye bath temperature increasing gradually from 60° C to about 100° C over a period of 40 minutes, followed by further dyeing at about 100° C for 40 minutes. The cross-dyed portion of the resulting yarn shows no signs of stain, and the yarn is highly saleable.

In place of dyeing with the 1:2 type pre-metallized acid dye, the fiber to be first-dyed is treated under the following conditions: 5 percent o.w.f. cationic black dye used in Example 2, 10 percent o.w.f. sodium sulfate, 1 percent o.w.f. acetic acid, 1.8 percent o.w.f. cationic retarder, liquor ratio 1/20, with the dye bath temperature increasing gradually from 60° C to 85° C over a period of 40 minutes, followed by further dyeing at 85° C for an additional 10 minutes, and then increasing from 85° C to about 100° C over a period of 20 minutes, followed by further dyeing at about 100° C for 30 minutes. When the resulting yarn is processed as above, no beneficial effect of cross dyeing can be obtained, with the dye bleeding out from the first-dyed yarn and extensively staining the second-dyed yarn, the entire product assuming a uniform grayish shade.

## EXAMPLE 5

To 100 parts of a dyeing bath was added 0.3 part of the 1:2 type premetallized acid dye used in Example 2, and acrylic fiber B was dyed under the conditions set

forth in Table 1 for 2 hours. Soaping of the dyed fiber was carried out with 1 gram/liter of nonionic surface active agent, liquor ratio 1/20, temperature 60° C, time 30 minutes. The fiber was washed three times, each time with 50 times as much water as the fiber. Finally, the fiber is oiled and dried. The results of the above dyeing are summarized in Table 1.

Table 1

| No. | Dyeing conditions: Bath temperature (°C) | Salt added | Liquor ratio | Shade of dyed fiber, Y value (%) | Hue |
|---|---|---|---|---|---|
| I | 100 | None | 1/15 | 17.8 | Pale gray |
| II | 120 | None | 1/15 | 4.21 | Deep gray |
| III | 120 | 1 part of sodium sulfate | 1/15 | 1.42 | Near black |
| IV | 120 | 2 parts of sodium sulfate | 1/15 | 1.28 | Near black |
| V | 120 | 1 part of calcium chloride | 1/15 | 1.06 | Stark black |

The shade of the dyed fiber is expressed in Y (percent) which denotes the shade of a sample measured for tristimulus values on the basis of the blue-black standard plate (X: 2.90 percent, Y: 2.90 percent, Z: 5.55 percent) by means of a color differential meter (Japan Color Machines, Ltd., Model CM 20). The sample is substantially perfect black when its Y value is less than 1.10 percent.

It can be seen from Table 1 that under dyeing condition I, i.e., at the dye bath temperature of 100° C and in the absence of the salt, the fiber is dyed only a pale shade, but that when the dye bath temperature is 120° C as under condition II, the diffusion of the dye is promoted even in the absence of the salt, with the result that although the final shade is dark, rich gray, it is impossible to obtain a desired black product. It was possible to obtain nearly black fibers when the alkali metal salt added is sodium sulfate as in the case of conditions III and IV. Under condition V, i.e., when calcium chloride, which is a water-soluble divalent metal salt, is added, a substantially perfectly black fiber can be obtained.

Then 10 parts of the fiber dyed under dyeing condition V where mix-spun with 90 parts of undyed acrylic fiber B, and the resulting mottled sliver is dyed under the following conditions: 0.2 percent o.w.f. cationic dye, C.I. 42025, 1 percent o.w.f. acetic acid, 10 percent o.w.f. sodium sulfate, 3 percent o.w.f. cationic retarder, liquor ratio 1/50, the bath temperature gradually increasing from 60° C to about 100° C over 60 minutes, and the dyeing continued at about 100° C for an additional 30 minutes. The dyed fiber was washed with water, followed by drying. The final variegated dyed fiber was completely free from stain and the second-dyed portion of the same fiber assumed a bright, pale blue shade. Thus, there was obtained an extremely superior variegated dyed fiber.

On the other hand, the first-dyed fiber was prepared by dyeing acrylic fiber B by means of a package dyer under the following conditions: 5 percent o.w.f. cationic black dye used in Example 2, 1 percent o.w.f. sodium acetate, liquor ratio 1/20, with the dye bath temperature gradually increased from 60° C to about 100° C over 40 minutes, and the dyeing was further continued at about 100° C for another 90 minutes. The dyed fiber was then blended with undyed acrylic fiber B in the same manner as above. The resulting sliver was found to be extensively stained by the dye bleeding out from the first-dyed fiber, assuming an undesirable appearance.

## EXAMPLE 6

To 100 parts of a dyeing bath was added 0.33 part of 1:2 type pre-metallized acid dye, C.I. 17941, and 6.7 parts of acrylic fiber A were dipped in the bath. The dyeing was continued at 120° C for 2 hours. In carrying out this dyeing, the various water-soluble inorganic salts of Table 2 were added to portions of the above-mentioned bath, and the dyeing results were compared. The shades of the dyed samples were evaluated according to Kubelka-Munks's formula. The results, in K/S, are shown in Table 2.

Table 2

| Inorganic salt | Amount of inorganic salt (m.mole): Control (none) | 23.2 | 46.4 | 92.8 |
|---|---|---|---|---|
| | *K/S* | | | |
| Sodium chloride | 0.5 | 1.8 | 2.0 | 3.2 |
| Sodium sulfate | 0.5 | 1.6 | 2.4 | 3.7 |
| Barium chloride | 0.5 | 5.1 | 5.8 | 5.9 |
| Zinc chloride | 0.5 | 4.2 | 4.4 | 5.2 |
| Magnesium chloride | 0.5 | 4.1 | 4.2 | 4.9 |
| Calcium chloride | 0.5 | 5.0 | 5.4 | 6.0 |

The shade of the dyed fiber is represented by the *K/S* value, which is obtained by measuring the reflectivity *R* of the dyed fiber at a wavelength of 580 millimicrons, and then calculating *K/S* by means of the following equation:

$$K/S = (1 - R)^2/2R$$

When the dyeing is carried out in the absence of salt, the fiber is merely "stained," but the addition of salt promotes dyeing. In addition, while the fiber is dyed darker as the amount of salt is increased, irrespective of the type of salt, the employment of alkali salts such as sodium chloride, sodium sulfate, etc. gives *K/S* values ranging from 1.6 to 3.7 which are equivalent to pale to medium shades. When water-soluble divalent metal salts are added, the *K/S* values of the resulting fibers are at least equal to 4.0 or higher, that is, the fibers are dyed darker than medium shades.

On the other hand, slivers were prepared by mix-spinning 15 parts each of the dyed fibers prepared above with 15 parts each of undyed acrylic fiber B and the resulting slivers were made into knits. These knits were dyed under the following conditions: 0.4 percent o.w.f. cationic dye, C.I. 48035, 1 percent o.w.f. acetic acid, liquor ratio 1/50, with the dye bath temperature gradually increased from 60° C to 90° C over 30 minutes and the dyeing continued for an additional 60 minutes, at the end of which time the dyed articles were washed and dried. As for the final variegated dyed knits, the articles dyed in accordance with the present invention yielded superior dyed products having a brillantly variegated pattern of blue and orange-yellow.

## EXAMPLE 7

Acrylic fiber A was dyed for 120 minutes using a dye bath containing a 1:2 type pre-metallized acid dye and a watersoluble inorganic salt as shown in Table 3, at a liquor ratio of 1/20 and a temperature of 120° C. The fiber dyed this way, as well as undyed acrylic fiber A, was spun into slivers which are then mix-plied into a single sliver in which the two components were arranged in a symmetrical pattern, and this single sliver was further mix-plied to prepare a fiber with a mottled pattern. This fiber was then dyed under the following conditions: 0.5 percent o.w.f. cationic dye, C.I. 48055, 1 percent o.w.f. acetic acid, liquor ratio 1/100, with the bath temperature increased gradually from 60° C to 90° C over about 30 minutes, followed by boiling for another 60 minutes.

The degrees of staining of variegated dyed fibers prepared in the described manner are summarized in Table 3.

Table 3

| First-dyeing conditions | | | | Staining of first-dyed fiber by second dye | Staining of second-dyed fiber by bleeding-out of first dye |
|---|---|---|---|---|---|
| Dyestuff | | Salt added | | | |
| C.I. No. | Concentration (% owf) | Type | Concentration (% owf) | | |
| 17941 | 3 | $Na_2SO_4$ | 20 | 3 | 4 – 5 |
| do. | 3 | $BaCl_2$ | 20 | 4 | 4 – 5 |
| 15675 | 5 | $Na_2SO_4$ | 20 | 2 – 3 | 3 |
| do. | 5 | $BaCl_2$ | 20 | 4 | 3 – 4 |
| 15707 | 5 | $Na_2SO_4$ | 20 | 2 – 3 | 4 – 5 |
| do. | 5 | $BaCl_2$ | 20 | 4 | 4 – 5 |

It is apparent from Table 3 that in all cases there is substantially no staining due to the bleeding out of the first dye, but that the staining of the first-dyed fiber by the cationic dye used in the second dyeing is considerably alleviated by employing a water-soluble divalent metal salt.

The degree of staining was determined as follows. A dyed acrylic fiber and the same undyed acrylic fiber were precisely weighed at 1 g. each, and both fibers were put into the same beaker fitted with a reflux condenser and boiled for one hour at a liquor ration of 1/50. After this treatment, each of the two fibers was dried at a temperature below 60° C. The staining of the undyed fiber was evaluated by the AATCC Chart for Measuring Transference of Color or Geometric Staining Scale, and the values obtained were converted into series. The value 5 represents the best result, i.e., an absence of staining of the undyed fiber, and the degree of staining increases with a decrease in the numerical value. A reported value of, for example 2–3, indicates more staining than would be represented by the value 3, but less staining than would be represented by the value 2.

What we claim is:

**1.** In a process for preparing multi-colored acrylic fiber textile material which comprises dyeing a first textile material of an acrylic fiber containing an augmented number of acid groups but no basic groups, combining the dyed textile material with a second textile material of an undyed acrylic fiber containing an augmented number of acid groups but no basic groups by blending the dyed and undyed textile materials, and thereafter dyeing the resultant material with a cationic or disperse dye, the improvement according to which the dyeing of the first textile material is conducted at a temperature of at least 100° C in a first dye bath containing a dilute solution of a neutral dyeing 1:2 type pre-metallized acid dye and 0.5–5.0 percent by weight, based on the weight of the dye bath, of at least one salt selected from the group consisting of calcium chloride, barium chloride, zinc chloride, magnesium chloride, cadmium chloride, zinc sulfate, magnesium sulfate, zinc nitrate, cadmium nitrate and calcium thiocyanate.

**2.** The improvement as claimed in claim **1**, wherein the first textile material is dyed at 100°–130° C.

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