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3,788,805

PRODUCING MULTICOLOR DYED ACRYLIC TEXTILE CONTAINING WOOL WITH ACID, DIRECT AND CATIONIC DYES

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No Drawing. Filed Apr. 23, 1971, Ser. No. 137,005

Claims priority, application Japan, Apr. 27, 1970, 45/36,080

Int. Cl. D06p 3/82

U.S. Cl. 8—21 A

8 Claims

ABSTRACT OF THE DISCLOSURE

Process for obtaining multicolored textile products by blending a basic group-containing acrylic fiber and wool, dyeing the product with a direct dye at a pH of 5-9 to dye the acrylic fiber component, treating the entire dyed product with an anionic aromatic polycondensate containing dissociable groups, such as a naphthalenesulfonic acid-formaldehyde condensate, and then dyeing the product in a second bath with an acid dye at a pH of 2-5 to dye the wool component.

This invention relates to a process for producing acrylic multicolor dyed textile products containing wool and more particularly to a process for producing multicolor dyed textile products having two or more different color shades very remarkable in the multicolor contrasting effect by dyeing a textile product containing wool and an acrylic synthetic fiber (hereinafter referred to as "basic group-containing acrylic fiber") consisting of an acrylonitrile polymer or polymer composition with which is copolymerized a basic unsaturated monomer having a basic nitrogen atom showing a specific basicity in a dyeing bath of a pH of 5 to 9 by using a direct dye to dye only said basic group-containing acrylic fiber portion, then treating said textile product with an anionic active agent and then dyeing the wool portion in a different color in a dyeing bath under an acid condition by using an acid dye.

Prior to the present invention, there have been proposed various methods for producing multicolored textile products. For example, there has been proposed a method wherein two fibers previously dyed in respectively different colors are blended and spun into a multicolored yarn, which is then woven, knitted or otherwise organized into a multicolored textile product. Another known method comprises the steps of blending a dyed fiber and undyed fiber, spinning the resulting blend into a yarn, then dyeing the undyed fiber, prior to or subsequent to fabrication into a textile product, with a dye different in color from that employed for the previously dyed fiber. In still another method, fibers with different dyeing properties are blended, the blend is spun into a yarn, and then the yarn or an article made therefrom is dyed taking advantage of the different dyeing properties to yield a multicolored textile product.

However, it has been very difficult to develop a multicolor effect by multicolor dyeing with the same kind of dye a textile product of different fibers of the same dyeability, that is, a textile product prepared from different fibers showing a dyeing activity with the same kinds of dyes. Further, it has been difficult to produce a multicolor dyed textile product by combining such fibers dyeable with the same kinds of dyes with various other fibers. For example, even if a knitted or woven fabric containing a basic group-containing acrylic fiber and wool is dyed in different colors in two baths with anionic dyes showing a dyeing activity on said two kinds of fibers, the dye in the later dyeing stains the prior dyed fiber, and on the

other hand, the dye seeps out of the prior dyed fiber and stains the later dyed fiber. Therefore, the multicolor contrasting effect is remarkably impaired.

We have now found that, in a process for producing a multicolored textile product by a multicolor dyeing method in two steps in two baths, a textile product containing a basic group-containing acrylic fiber and wool, when the above mentioned basic group-containing acrylic fiber is made to contain, as a polymer component, a basic unsaturated monomer having a specific basicity, acting as a dye site is prior dyed in a particular dyeing pH range by using a direct dye, and then is treated with an anionic active agent, even if said dyed fiber is left to soak in boiling water for a long time, substantially no phenomenon of seeping out of the dye (so-called bleeding) is recognized. Further, said fiber is not stained at all with the dye having a dyeing activity on said fiber and being present in the later dyeing bath.

A main object of the present invention is to obtain a multicolor dyed textile product having two or more different colors, being excellent in the multicolor contrasting effect.

An object of the present invention is to obtain a multicolor dyed textile product having no inter-staining at all, by multicolor dyeing in two steps in two baths a textile product containing a basic group-containing acrylic fiber and wool.

Other objects of the present invention will become clear from the concrete explanation of the present invention described in the following.

The above mentioned objects of the present invention are attained by dyeing a textile product containing an acrylic fiber consisting of an acrylonitrile polymer or polymer composition made to contain, as a polymer component, a basic unsaturated monomer which has a pK_b value at 25° C. of less than 8.0, and wool in a dyeing bath of a pH of 5 to 9 by using a direct dye to dye only said acrylic fiber portion, then treating said textile product with an anionic active agent (selected essentially from aromatic polycondensation products containing sulfonic acid groups) and then dyeing said wool portion in a different color in a dyeing bath under an acid condition by using an acid dye.

That is to say, in such multicolor dyeing method in two steps in two baths according to this invention, only the acrylic fiber containing a basic unsaturated monomer having a specific basicity is dyed with a direct dye under a specific condition and the obtained dyed fiber-containing textile product is treated with an anionic active agent so that the direct dye deposited on said dyed fiber may be prevented from bleeding out into the dyeing bath, and at the same time the acid dye used in the later dyeing may be prevented from staining said dyed fiber. Then, only the wool portion contained in the above textile product is dyed in a different color in a specific pH range by using the acid dye.

Thus, in the method of the present invention, after a basic group-containing acrylic fiber and wool having a dyeing activity with the same kind of dye are spun, knitted or woven to be formed into a textile product, a very excellent multicolor contrasting effect is developed in said textile product and such novel effect as can never be conceived in any known conventional multicolor dyeing method is obtained. That is to say, it has been considered to be very difficult to develop a multicolor contrasting effect in fibers showing a dyeing activity with the same kind of dye. However, according to the invention, it has become possible to obtain a multicolor dyed textile product having an excellent multicolor contrasting effect and being favorable in its aesthetic performance without causing any staining and bleeding out, in two kinds of fibers

showing a dyeing activity with the same kind of dye by selecting an acrylic fiber containing a basic unsaturated monomer showing a specific basicity and selecting a specific prior dyeing condition, specific treatment of the prior dyed fiber and specific later dyeing condition.

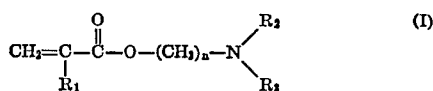
The basic group-containing acrylic fiber and wool to be used in the present invention are subjected to such spinning, knitting or weaving operation as blending, mix-spinning, mix-plying, blend-weaving or blend-knitting together with or without such other (as a third component) as, for example, an acrylic fiber containing dissociable acid groups or polyester fiber, so as to be formed into a textile product such as spun yarn or knitted or woven fabric. Then the multicolor dyeing method according to the present invention is applied to such textile product.

As the first or prior dyeing condition with a direct dye in the present invention, there may be used a general known dyeing recipe, except the dyeing bath pH should be a range of 5 to 9, preferably 6 to 8. For the second or later dyeing condition with an acid dye there may be used a general known dyeing recipe except that the dyeing bath pH should be acid, preferably in a range of 2 to 5.

The direct dyes and acid dyes (including pre-metallized acid dyes) may be any of the commercial ones. Particular examples of direct dyes are those under such C.I. names as C.I. Direct Yellow, C.I. Direct Orange, C.I. Direct Red, C.I. Direct Violet, C.I. Direct Blue, C.I. Direct Green, C.I. Direct Brown and C.I. Direct Black. Particular examples of acid dyes are those expressed under such C.I. names as C.I. Acid Yellow, C.I. Acid Red, C.I. Acid Blue, C.I. Acid Brown, C.I. Acid Orange, C.I. Acid Violet, C.I. Acid Green, C.I. Acid Black, etc.

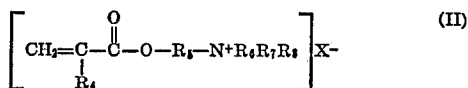
The C.I. names as used above and in the examples to be given hereinafter are those of Colour Index, 2nd edition, 1956, and Supplement, 1963, published by The Society of Dyers and Colourists, Bradford, England and The American Association of Textile Chemists and Colorists, Lowell, Mass., U.S.A.

The basic group-containing acrylic fiber to be used in the present invention is an acrylic synthetic fiber prepared by an ordinary spinning process from an acrylonitrile polymer or composition (simple polymer or polymer blend) made to contain, as a polymer component, basic unsaturated monomer of a pK_b value at 25° C. of less than 8.0, preferably less than 7.5, such as, for example, a basic unsaturated monomer having a basic nitrogen atom, as an unsaturated monomer represented by the below mentioned General Formula I:



wherein R_1 represents hydrogen or methyl group, each of R_2 and R_3 represents methyl or ethyl group and n represents an integer of 2 to 4,

or the General Formula II



wherein R_4 represents hydrogen or methyl group, R_5 represents an alkylene group of 2 to 4 carbon atoms, hydroxyalkylene group or $(-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-)$ group, each of R_6 , R_7 and R_8 represents methyl, ethyl or propyl group and X represents an anion, or unsaturated monomer such as a quaternary product of such nitrogen-containing heterocyclic unsaturated compound as an N-vinylimidazolic compound or vinylpyridine. Thus the nitrogen group-containing acrylic polymer or polymer composition means:

(1) acrylonitrile copolymer consisting of acrylonitrile and the above explained basic unsaturated monomer

and, if desired, one or more neutral ethylenically unsaturated monomers, or

(2) polymer blend consisting of (a) homopolymer of the above explained basic unsaturated monomer or copolymer thereof with other copolymerizable unsaturated compound (including acrylonitrile and neutral monoethylenically unsaturated monomer) and (b) acrylonitrile homopolymer or copolymer.

Examples of the above mentioned neutral monoethylenically unsaturated monomer are esters (e.g. methyl, ethyl, propyl, butyl, etc. esters) of acrylic acid and methacrylic acid; vinyl esters of carboxylic acids, such as vinyl formate, vinyl acetate, etc.; acrylamide, methacrylamide and derivatives thereof; vinyl or vinylidene halides such as vinyl chloride, vinyl bromide, vinylidene chloride, etc.; styrene, cyanostyrene, etc.

It is preferable that the copolymer or polymer blend for forming the basic group-containing acrylic fibers contains at least 75% by weight of acrylonitrile, 0.5-10% by weight of the basic unsaturated monomer(s) and 0-15% by weight of the neutral monoethylenically unsaturated monomer(s).

If an acid unsaturated monomer containing an acid dissociable group such as sulfonic acid group or carboxyl group is contained, as copolymerized, in the acrylonitrile copolymer forming the above mentioned basic group-containing acrylic fiber, the effect of the present invention will be reduced. Therefore, the use of such acid monomer should be avoided.

However, when persulfate, sulfite or bisulfite is used in the polymerization initiator system in producing said copolymer, a slight amount of such dissociable acid group as sulfuric acid group or sulfonic acid group will be introduced into the terminal portions of the above mentioned basic group-containing acrylic fiber-forming polymer, but this will have no influence on the effect of the present invention.

The symbol pK_b used in this invention means electric dissociation exponent and its relation with the electric dissociation constant (ionization constant) K of said basic unsaturated monomer is as follows:

$$pK_b = -\log_{10}K$$

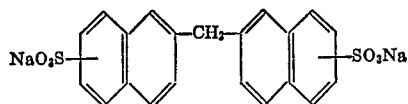
The acrylic fiber containing dissociable acid groups to be blended, mix-twisted, blend-woven or blend-knitted, as required, together with a basic group-containing acrylic fiber and wool is a fiber dyeable with a cationic dye and formed from an acrylonitrile polymer or copolymer into whose molecular terminal such dissociable strong acid group as a sulfuric acid group or sulfonic acid group is introduced by using persulfate, sulfite or bisulfite in the polymerization initiator system, in a step of producing an acrylonitrile homopolymer or copolymer, or in which a dissociable acid group has been introduced by the copolymerization with acrylonitrile of an unsaturated monomer containing such sulfonic acid group as of styrenesulfonic acid, vinylsulfonic acid, allylsulfonic acid or methallylsulfonic acid or its salt, or such carboxylic acid group as of acrylic acid, methacrylic acid or itaconic acid or its salt. The above described basic unsaturated monomer is not contained, as copolymerized, in said fiber forming polymer.

It is preferable that the copolymer for forming the acrylic fibers containing dissociable acid groups contains at least 80% by weight of acrylonitrile, 0.01-5% by weight of said unsaturated monomer containing sulfonic acid groups or carboxylic acid groups and 0-15% by weight of at least one neutral monoethylenically unsaturated monomer.

The anionic active agent to be used in the present invention is an anionic aromatic polycondensate containing dissociable acid group such as sulfonic acid group, for

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example, a naphthalenesulfonic acid formaldehyde condensate represented by the chemical formula:



water-soluble product obtained by reacting a formaldehyde condensate of a polyhydric phenol carboxylic acid with a sulfite (Japanese patent publication No. 7,044/1968); sulfomethylate of a condensation product of di(4-hydroxyphenyl)-sulfone and a lower aliphatic aldehyde (Japanese patent publication No. 24,205/1968); water-soluble polycondensate obtained by heating bisphenol sulfone or its derivative and an aromatic sulfonic acid in an acidic condition in the presence of formaldehyde (Japanese patent publication No. 10,424/1966); aqueous solution of an alkali salt or ammonium salt of a condensation product of a lower aliphatic aldehyde and a sulfonic acid of dioxydiphenyl sulfone (Japanese patent publication No. 23,231/1965); reaction product of 2,2'-bis(hydroxyphenyl)sulfone and oxymethane sulfonic acid (French Pat. No. 1,274,939); bis(4,4'-dihydroxyphenyl)sulfone as sulfonated and condensed with formaldehyde (British Pat. No. 975,307) or trimethylol monomethanesulfonic acid compound of 4,4'-diphenyldimethylmethane (U.S. Pat. No. 2,522,569).

In the case of treating a textile product containing wool and a dyed acrylic synthetic fiber consisting of an acrylonitrile copolymer containing the above mentioned basic group-containing unsaturated monomer with a treating solution of at least one of such anionic active agents as are described above, proper values of the amount of use of the treating agent and the treating conditions (such as the pH and temperature) are to be determined depending on the kind of treating agent. However, generally, the treating solution contains 0.5-10%, preferably 1-5% by weight of the anionic active agent based on the weight of the dry fiber, and is adjusted to an acidic state, preferably at a pH of 2-7. Further, in order to promote the treating effect it is necessary to conduct the treatment at a temperature above 60° C.

In order to adjust the pH of the treating bath, there may be used such organic or inorganic acid as acetic acid, oxalic acid, formic acid, hydrochloric acid, sulfuric acid or nitric acid.

In order that the present invention may be better understood, typical examples of the present invention are shown in the following. In the examples, all the percentages and parts are based on weight unless otherwise specified, and percent O.W.F. means the percentage by weight on the dry fiber.

EXAMPLE 1

A spun yarn of 36's/2 was made of an acrylic fiber (which will be referred to as "fiber A" hereinafter) consisting of an acrylonitrile copolymer containing 90% acrylonitrile, 7% vinyl acetate and 3% N,N-dimethylaminoethyl methacrylate of a pK_b value of 6.8 as basic group-containing acrylic fiber. Two kinds of spun yarns (36's/2) were made respectively of an acrylic fiber made from an acrylonitrile copolymer consisting of 90% acrylonitrile, 9.7% methyl acrylate and 0.3% sodium allyl sulfonate (which will be referred to as "fiber B"), which was a basic dye-dyeable acrylic fiber, and wool. The obtained three kinds of spun yarns were blend-knitted in the form of stripes to obtain plain knits.

The thus obtained knit fabric was heated in the first bath at a rate of 1° C./min. from 60° C. to about 100° C. and then kept at about 100° C. for 30 minutes at a recipe of 2% O.W.F. (on the fiber A) of C.I. Direct Blue 78 (C.I. 34200), a pH of 7.0 (adjusted with sodium acetate) and a liquor ratio of 1/50 to dye the fiber A portion. Then the fabric was treated at 100° C. for 45 minutes at a recipe of 2% O.W.F. (on the fiber A) of an

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anionic active agent, a pH of 3.0 (adjusted with sulfuric acid) and a liquor ratio of 1/50 in the same bath.

The above anionic active agent was that prepared as follows. Thus, 265 parts of bisphenol sulfone and 220 parts of beta-naphthalene sulfonic acid were mixed together. To this mixture was added 2 parts of concentrated sulfuric acid and further slowly added 105 parts of 30% aqueous solution of formaldehyde. The mixture was stirred for 2 hours at 110° C. to cause reaction. Then the mixture was neutralized and added with saturated sodium sulfate aqueous solution to salt-out the polycondensate, which was recovered and dried. The dried powder was used as the anionic active agent.

Then, the knit fabric thus treated with the anionic active agent was dyed in another bath. Thus, at a recipe of 1% O.W.F. (on the fiber B) of C.I. Basic Yellow 11, (C.I. 18820), 3% O.W.F. (on the wool) of C.I. Acid Red 118, 1 g./l. of Noigen ET-170 (nonionic dispersing agent, 3% O.W.F. (on the fiber B) of Levenol R (cationic retarder), a pH of 3.0 (adjusted with sulfuric acid) and liquor ratio of 1/50, the bath was heated at a rate of 2° C./min. from 60° C. to 80° C., maintained at 80° C. for 15 minutes, then heated to about 100° C. during 15 minutes and was kept at that temperature for 45 minutes to dye the fiber B portion as well as the wool portion.

In the thus obtained dyed knit fabric, no interstaining of the three kinds of fibers with one another was recognized at all, and the red-yellow-blue stripe tone was very beautiful.

EXAMPLE 2

A fabric was made by using blended spun yarns (of 30's/2) obtained from 15 parts of wool and 85 parts of the fiber A as warps and using blended spun yarns (of 30's/2) obtained from 15 parts of wool and 85 parts of the fiber B as wefts. Then the fabric was first dyed in the fiber A portion under the same conditions as in Example 1 at a recipe of 2% O.W.F. (on the fiber A) of C.I. Direct Brown 84, a pH of 7.0 (adjusted with Na_2SO_3) and a liquor ratio of 1/50 in the first bath and was then treated at about 100° C. for 45 minutes at a pH of 3.0 (adjusted with sulfuric acid) in the same bath, to which 3% O.W.F. (on the fiber A) of anionic active agent (a high molecular weight condensate of an aromatic sulfonic acid) has been added.

Then, in the second bath containing 1% O.W.F. (on the fiber B) of C.I. Basic Red 18 (C.I. 11085) and 1.5% O.W.F. (on the wool) of C.I. Acid Blue 82, the fabric was dyed in the wool and fibers B with the same process as Example 1.

The thus obtained dyed fabric was a sprinkly colored yarn in which no inter-staining of the three kinds of fibers with one another was recognized at all, and the aesthetic performance was very favorable.

EXAMPLE 3

When the multicolor dyeing operation in Example 1 was repeated by using an acrylic fiber consisting of an acrylonitrile copolymer containing 91% acrylonitrile, 6% methyl acrylate and 3% N,N-diethylaminoethyl methacrylate of a pK_b value of 6.6, or an acrylic fiber consisting of a polymer mixture of 10 parts of an acrylonitrile copolymer of 82% acrylonitrile and 18% of 2-hydroxy-3-methacryloxypropyltrimethylammonium chloride of a pK_b value of less than 1 and 115 parts of an acrylonitrile copolymer of 90% acrylonitrile and 10% methyl acrylate instead of the fiber A in Example 1, there was obtained a multicolor dyed product which had a very favorable multicolor contrasting effect and in which no inter-staining of the fibers was recognized at all.

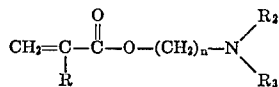
What we claim is:

1. A process for producing a multicolor dyed acrylic textile product containing wool, which comprises dyeing a textile product containing wool and an acrylic fiber consisting essentially of an acrylonitrile polymer or poly-

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mer composition, bath containing, as a polymer component, a basic unsaturated monomer having a pK_b value at 25° C. of less than 8.0, with a direct dye at a pH of 5 to 9 to dye the acrylic fiber portion of the textile product, treating the dyed textile product with an anionic aromatic polycondensate containing sulfonic acid groups and dyeing the wool portion of the textile product with an acid dye, having a different color than the direct dye, at a pH of 2 to 5.

2. The process as claimed in claim 1 wherein the acrylic fiber is prepared from a copolymer containing at least 75% by weight of acrylonitrile, 0.5-10% by weight of at least one compound of the formula



wherein R_1 is hydrogen or methyl, each of R_2 and R_3 is methyl or ethyl, n is an integer of 2-4, and 0-15% by weight of at least one neutral monoethylenically unsaturated monomer.

3. The process as claimed in claim 1 wherein the basic unsaturated monomer has a pK_b value of less than 7.5.

4. The process as claimed in claim 1 wherein the dyeing with the direct dye is conducted at a pH of 6-8.

5. The process as claimed in claim 1 wherein the anionic active agent is a water-soluble polycondensate obtained by heating bisphenol sulfone and an aromatic sulfonic acid in the presence of formaldehyde and an acid.

6. The process as claimed in claim 1 wherein the treatment with the polycondensate is conducted by treating the textile product with an aqueous acidic solution of pH 2-7 containing said polycondensate in an amount of 0.5-10% on the weight of the dry fiber at a temperature above 60° C.

7. A process for producing a multicolor dyed acrylic textile product, which comprises dyeing a textile product

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consisting essentially of (a) acrylic fibers prepared from an acrylonitrile polymer or polymer composition, both containing, as a polymer component, a basic unsaturated monomer having a pK_b value at 25° C. of less than 8.0, (b) wool and (c) acrylic fibers having dissociable acid groups, in a dye bath having a pH of 5 to 9 with a direct dye, treating the dyed textile product with an anionic aromatic polycondensate containing sulfonic acid groups and dyeing the thus-treated textile product in a dye bath having a pH of 2 to 5 and containing an acid dye and a cationic dye.

8. The process as claimed in claim 7 wherein the acrylic fibers having dissociable acid groups are prepared from a copolymer comprising at least 80% by weight of acrylonitrile, 0.01-5% by weight of an unsaturated monomer containing sulfonic acid group or carboxylic acid group and 0-15% by weight of at least one neutral monoethylenically unsaturated monomer.

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GEORGE F. LESMES, Primary Examiner

P. C. IVES, Assistant Examiner

U.S. Cl. X.R.

8-25, 168, 172, 177 AB

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,788,805 Dated January 29, 1974

Inventor(s) Tomoji OOKUBO, Kiyoshi HASHIMOTO and Masaru OKADA

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 7, line 1, change "bath" to --both--.

Signed and sealed this 24th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents