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DYEING WITH LEUCO-VAT DYE ESTERS POLY- PROPYLENE FIBERS AND CELLULOSIC FIBER UNIONS THEREWITH

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This invention relates to a process for dyeing fibers of stereoregular polypropylene. More particularly, this invention relates to a process for dyeing stereoregular polypropylene fibers with vat dyestuffs.

One of the new fibers that has been introduced recently to the trade is made from stereoregular polypropylene, a highly crystalline polymer that melts in the range of about 165° to 172° C. Stereoregular polypropylene filamentary articles have potentially wide application in the domestic as well as in the industrial market, since they possess excellent physical properties, such as, for example, excellent tenacities, superior fatigue and abrasion resistance, and the like. However, in order for stereoregular polypropylene filamentary articles to enjoy widespread use, it is necessary that such articles be dyeable in a wide range of colors which are reasonably color fast when subjected to washing and/or dry cleaning treatments, and are also reasonably stable to light.

The dyeing of polypropylene fiber, however, has been recognized as an especially difficult problem because of the extremely hydrophobic nature of stereoregular polypropylene and the absence of functional groups in its structure which can serve as "dye sites" to enable dyestuffs to become firmly attached to the fibers. The dyeing of stereoregular polypropylene fiber, therefore, presents special problems and difficulties which must be overcome. This is particularly true with respect to attempts to dye such fibers with vat dyestuffs, since conventional methods for dyeing cotton and cellulosic materials with vat dyestuffs from an alkaline vat are not satisfactory because the highly hydrophobic stereoregular polypropylene fibers have little or no affinity for vat dyes applied thereto from an alkaline vat.

Limited success in dyeing stereoregular polypropylene fibers with vat dyes has been achieved using known vat acid techniques by contacting the fibers in an acidified dye bath with leuco vat dyestuffs in vat acid form, and subsequently subjecting the dye contacted fibers to oxidizing conditions to develop the oxidized form of the dye. Such dyeings, however, are often deficient with respect to levelness of dyeing.

The primary object of the present invention, therefore, is to provide an improved process for obtaining level dyeing of stereoregular polypropylene with vat dyestuffs. Other objects and advantages will be apparent from the description of the invention.

In accordance with this invention, stereoregular polypropylene fibers are dyed to substantially color fast level shades by subjecting said fibers, prior to dyeing, to treatment with an aqueous solution containing a reducing agent for vat dyestuffs effective in neutral and acid solution, contacting the thus pretreated fibers with an acidified aqueous dyebath containing, in addition to dye selected from the group consisting of the sulfuric acid esters of leuco vat dyestuffs, a reducing agent for said dye effective in neutral and acid solution, dyeing said fibers at the boiling point of the dyebath, and subsequently subjecting the dyed fibers to oxidizing conditions to develop the oxidized form of the dye.

In preferred embodiments of the invention, stereo-

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regular polypropylene fibers in the form of filaments, threads, yarns, cords or fabric woven from such fibers are given a preliminary conventional scouring treatment in an aqueous detergent or soap bath to remove residual spinning and weaving lubricants and sizing agents. The scoured fibers are then pretreated in a solution of a reducing agent for vat dyestuffs effective in neutral and acid solution, such as sodium formaldehyde sulfoxylate, and the thus pretreated fibers are contacted with an acidified dye bath containing, in addition to dye selected from the class consisting of the sulfuric acid esters of leuco vat dyes, a reducing agent for vat dyestuffs effective in neutral and acid solution, such as sodium formaldehyde sulfoxylate, and preferably a dispersing agent effective in acid solution, whereupon the temperature of the dyebath is raised to the boiling point and maintained at the boiling point for sufficient time to dye the fibers. The dyed fibers are then subjected to oxidizing conditions to develop the oxidized form of the dye, preferably in a separate developing bath. After oxidation the dyed fibers are rinsed, given a conventional soaping or scouring treatment in an aqueous detergent or soap bath, rinsed and dried.

It has been found that dyeing of stereoregular polypropylene fibers with vat ester dyes in accordance with this invention differs in several respects from the dyeing of other known synthetic hydrophobic fibers with vat ester dyes. These differences have been found to be necessary and important in the dyeing of stereoregular polypropylene fibers with vat ester dyes in order to obtain level dyeing of the fibers. More specifically, it has been found that the polypropylene fibers should be pretreated with a solution of a reducing agent for vat dyestuffs effective in neutral and acid solution prior to dyeing. Other known synthetic fibers do not require such pretreatment. Moreover, it has also been found that the presence of a reducing agent for vat dyes effective in neutral and acid solution, such as sodium formaldehyde sulfoxylate, in the dyebath will improve the leveling of the dye on the fibers and maintain the dye in a reduced state during dyeing. This practice is not customary in dyeing other synthetic hydrophobic fibers with vat ester dyes. Another difference between preferred practice of this invention and customary dyeing practice with vat ester dyes is that dyeing in accordance with this invention is carried out at the boiling point of the dyebath, whereas customarily the dyebath is employed at temperatures substantially below the boiling point.

The general nature of the invention having been set forth, the following examples illustrate some specific embodiments of the invention. It is to be understood, however, that the invention is in no way limited to the examples, since this invention may be practiced by the use of various modifications and changes within the scope of the invention as described herein.

EXAMPLES 1-11

The fabric employed in these examples was knit from 210 denier, 35 filament, stereoregular polypropylene yarn (6 denier per filament). Initially the fabric was scoured at a 40 to 1 liquor/fabric ratio by weight for 30 minutes at boiling temperature in an aqueous scouring bath containing 2%, based on fabric weight, of Triton X-100, a typical nonionic alkylaryl polyether alcohol surface active agent, and 1%, based on fabric weight, of soda ash.

The scoured fabric was then pretreated at a 40 to 1 liquor/fabric ratio for 15 minutes at 125° F. in a solution containing 10% (O.W.F.) of sodium formaldehyde sulfoxylate and also containing 0.1% by weight of Cal-solene Oil HSA, a sulfated ester detergent.

The dye baths for all examples were prepared as follows:

Ratio of dye liquor to fabric (by weight).....	40/1.
Sodium chloride.....	10% (O.W.F.).
Calsolene Oil HSA, a sulfated ester detergent.....	2% (O.W.F.).
Sodium formaldehyde sulfoxylate.....	2% (O.W.F.).
Sulfuric acid.....	1% (O.W.F.).
Sulfuric acid ester of leuco vat dye.....	2% (O.W.F.).

NOTE.—"O.W.F." means "based on weight of fabric."

The sulfuric acid esters of leuco vat dyes employed in these examples were commercially available products, and were obtained as the water soluble sodium salts of the sulfuric acid esters of leuco vat dyes.

In each example a specimen of the above scoured and pretreated fabric was introduced wet from the pretreating bath into the respective dye bath at room temperature, whereupon the dye bath was heated to boiling in 30 to 40 minutes with continuous agitation, and boiling and agitation were continued for one hour. The fabric specimens were then removed from their respective dye baths and were subjected to oxidation in an aqueous developing bath containing 1%, based on fabric weight, of sodium nitrite and 2%, based on fabric weight, of sulfuric acid at a 40 to 1 developing bath to fabric ratio for ten minutes at 125° F.

After oxidation the fabric specimens were rinsed and then soaped off in 0.1% by weight Triton X-100 solution at 160° to 170° F., again rinsed and dried.

Table I following lists pertinent data with respect to the dye used in each example, the color of the dyed fabric obtained, washfastness, resistance to extraction in perchloroethylene, and color stability to Fadeometer exposure.

Table I

Example No.	Dye		Color of Dyed Fabric	Wash fastness of Dyed Fabric ²	Resistance of Dyed Fabric to Perchloroethylene Extraction ³	Color Stability of Dyed Fabric to Fadeometer Exposure
	Commercial Designation	Color Index Designation ¹				
1.....	Calco Soluble Vat Blue 2B.	Soluble Vat Blue 5.	light blue.....	excellent..	no change.....	sl. break—40 hrs.
2.....	Calco Soluble Vat Scarlet HB.	Soluble Vat PR 107.	medium pink.....	do.....	moderate change..	Do.
3.....	Calco Soluble Vat Pink FF.	Soluble Vat Red 1.	do.....	do.....	slight change.....	mod. break—40 hrs.
4.....	Calco Soluble Vat Orange R.	Soluble Vat Orange 5.	light orange.....	do.....	do.....	sl. break—40 hrs.
5.....	Calco Soluble Vat Violet 6E.	Soluble Vat Violet 2.	medium violet.....	do.....	no change.....	sl. break—100 hrs.
6.....	Calco Soluble Vat Brown RR.	Soluble Vat Brown 5.	medium tan.....	do.....	slight change.....	mod. break—40 hrs.
7.....	Calco Soluble Vat Yellow GC.	Soluble Vat Yellow 2.	medium yellow.....	do.....	no change.....	no break—60 hrs.
8.....	Calco Soluble Vat Jade Green.	Soluble Vat Green 1.	medium green.....	do.....	do.....	no break—100 hrs.
9.....	Calco Soluble Vat Gray.	Soluble Vat Black 22.	dark gray.....	do.....	do.....	no break—80 hrs.
10.....	Ahcovat Soluble Blue IBC.	Soluble Vat Blue 6.	deep blue.....	do.....	do.....	no break—60 hrs.
11.....	Ahcovat Soluble Green IB.	Soluble Vat Green 1.	medium green.....	do.....	do.....	Do.

¹ The Colour Index, 2d Ed., Part I, edited by J. Barritt et al., published jointly by Society of Dyers and Colourists and A.A.T.C.C. (1956-58).

² Dyed fabric specimens scoured at 40/1 ratio of scouring bath to fabric by weight for 30 minutes at 160° to 170° F. in a 0.1% by weight for 30 minutes at 160° to 170° F. in a 0.1% by weight Triton X-100 solution.

³ Dyed fabric specimens extracted for 2 hours at room temperature with agitation in perchloroethylene.

EXAMPLE 12

Specimens of knit fabric made from 40 s spun yarn composed of a mixture of 65% by weight of stereoregular polypropylene fiber and 35% by weight of cotton fiber were dyed, respectively, with Calco Soluble Vat Blue 2B, with Calco Soluble Vat Scarlet HB, and with Calco Soluble Vat Yellow GC following substantially the same procedure described above for Examples 1-11. Very satisfactory union dyeing of the mixture of polypropylene and cotton fibers was obtained with each dye, and the dyed fabric specimens had substantially the same wash fastness, resistance to perchloroethylene extraction, and

light stability as shown by the dyed fabric in Examples 1, 2 and 7.

EXAMPLE 13

Specimens of knit fabric made from 40 s spun yarn composed of a mixture of 65% by weight of stereoregular polypropylene fiber and 35% by weight of viscose rayon fiber were dyed, respectively, with Calco Soluble Vat Blue 2B, with Calco Soluble Vat Scarlet HB, and with Calco Soluble Vat Yellow GC following substantially the same procedure described above for Examples 1-11. Very satisfactory union dyeing of the mixture of polypropylene and viscose rayon fibers was obtained with each dye, and the dyed fabric specimens had substantially the same wash fastness, resistance to perchloroethylene extraction, and light stability as shown by the dyed fabric in Examples 1, 2 and 7.

EXAMPLE 14

Three (3) parts by weight of fabric knit from 210 denier, 35 filament, stereoregular polypropylene yarn was initially scoured at a 40 to 1 liquor/fabric ratio by weight for 30 minutes at boiling temperature in an aqueous scouring bath containing 0.1% by weight of Triton X-100, a typical nonionic alkylaryl polyether alcohol surface active agent.

The scoured fabric was then treated in the following bath for 20 minutes at 50° C.:

0.3 part by weight of sodium chloride
0.06 part by weight of Calsolene Oil HSA, a sulfated ester detergent
0.06 part by weight of sodium sulfoxylate formaldehyde
150.0 parts by weight of water

whereupon six-hundredths (0.06) part by weight of Calco Soluble Vat Blue 2B (Colour Index 67301) was dissolved in a small amount of water and was added to the above

bath, and the temperature of the bath was raised to 100° C. and held at that temperature for 30 minutes. Three hundredths (0.03) part by weight of sulfuric acid was then added and dyeing was continued for an additional 30 minutes at 100° C.

The fabric was then removed from the dye bath and was subjected to oxidation treatment at 50° C. for 10 minutes in a developing bath containing:

0.03 part by weight of sodium nitrite
0.03 part by weight of sulfuric acid
150.0 parts by weight of water

The dyed fabric was soaped off in a 0.1% by weight

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solution of Triton X-100 at 70° C. for 10 minutes, rinsed and dried.

The fabric was dyed to a level shade of blue having substantially the same wash fastness, resistance to perchloroethylene extraction and light stability as shown by the dyed fabric in Example 1.

From the foregoing description it will be seen that practice of this invention requires dyes selected from the group consisting of the sulfuric acid esters of leuco vat dyestuffs, and any such dyestuff is suitable for the purposes of this invention.

The sulfuric acid esters of leuco vat dyestuffs are readily available on the market usually in the form of the alkali metal salts, such as those of sodium and potassium, or other water soluble or readily water dispersible salts such as those with a tertiary amine. They may be prepared, for example, by esterification of the reduced (leuco) form of the parent vat dye with chlorosulfonic acid in the presence of a tertiary amine. A substantial listing of available sulfuric acid esters of leuco vat dyestuffs appears under the subheadings "Vat Esters" for vat dyestuffs classified by Colour Index names on pages 346-350, Technical Manual of the American Association of Textile Chemists and Colorists, volume XXXVI (1960). These vat esters suitable for use in this invention are derived from both quinoid and indigoid types of vat dyestuffs by various methods and with the use of various assistants disclosed in the prior art, and are available in a wide range of colors. For the purposes of this invention the sulfuric acid esters of leuco vat dyes of the indigoid type are preferred, since in general these lead to more level dyeings. The dye employed may be a single vat ester dye or any mixture of vat ester dyes depending upon the color and shade desired.

The process of this invention is applicable to fiber of stereoregular polypropylene in the form of staple or continuous filament and may be applied to the fiber as individual filaments or as skeins of yarn, threads, cords, or fabric woven from such fiber. Blends in any proportion of stereoregular polypropylene fiber and cotton fiber, or of stereoregular polypropylene fiber and regenerated cellulose fiber can also be union dyed by the process.

The amount of dye employed can be varied as desired from as little as 0.1%, or less, based on fiber weight, to as much as 5% or more, depending largely on the depth of color desired, it being apparent that depth of color increases with increasing amount of dye employed.

Practice of this invention to obtain level dyeing requires that the stereoregular polypropylene fibers be subjected, prior to dyeing, to a pretreatment with a reducing agent for vat dyestuffs effective in neutral and acid solution. This is accomplished with an aqueous solution of a reducing agent such as sodium formaldehyde sulfoxylate, or an equivalent reducing agent for vat dyes. The amount of such reducing agent is not important, but will generally range between about 1% and about 15% based on fiber weight. A small amount on the order of about 0.1% by weight, of a nonionic surface active agent is generally employed in this pretreatment bath to promote uniform pretreatment of the fiber. Pretreatment is carried out at any temperature up to the boiling point of the pretreatment bath, and for a time sufficient to insure uniform pretreatment of the fibers. Usually a few minutes, from about 5 minutes to about 30 minutes at a temperature between about 125° F. and about 175° F. are sufficient for this purpose.

It has also been found that a reducing agent for vat dyestuffs effective in neutral and acid solution should be present in the dyebaths of this invention in order to obtain level dyeings. Such reducing agents are well known and readily available. Sodium formaldehyde sulfoxylate is very effective for this purpose. However, the invention is not limited in this respect, since any reducing agent for vat dyes effective in neutral and acid solution, such as zinc formaldehyde sulfoxylate or thio

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urea dioxide may also be used. The amount of such reducing agent should be sufficient to maintain the dye in its reduced (leuco) form, and may range from about 1%, based on fabric weight, to about 5%, based on fabric weight. Generally, a quantity of reducing agent about equal in weight to dyestuff employed is sufficient.

The dyebaths of this invention are acidified, and are, therefore, at a pH below 7, preferably between a pH of about 4 and a pH of about 6. This, coupled with the use of reducing agent for vat dyestuff effective in neutral and acid solution in the dyebath, insures that the dyestuff will remain in a form which has affinity for the stereoregular polypropylene fiber, and therefore, promotes satisfactory dyeing of the fibers. Moreover, dyeing is carried out at the boiling point of the dyebath. This also promotes level dyeing and optimum absorption of dyestuff by the stereoregular polypropylene fiber.

The dyebaths of this invention preferably contain a dispersing agent effective in acid solution, preferably a nonionic type, such as an alkylaryl polyether alcohol surface active agent. Other suitable dispersing agents effective in acid solution include, by way of example, alkylaryl sulfonates, such as higher alkyl benzene sulfonates, sulfonated condensation products of naphthalene and formaldehyde, isopropyl- and isobutyl-naphthalene sulfonates, and aliphatic or alicyclic sulfonates, such as N-oleyl-N-methyltaurine, higher alkyl esters of sulfosuccinic acid, sulfonated rosin or its derivatives, or lignin sulfonates.

Following the dyeing step, the dyed fibers are subjected to oxidizing conditions to develop the oxidized form of the dye. For this purpose any of the well known and conventional methods of oxidizing the dyed fibers can be employed, such as air oxidation with or without application of heat, treatment in an acidified aqueous alkali metal dichromate bath, or treatment in a dilute sulfuric acid bath containing sodium nitrite.

After development of the oxidized form of the dye, the dyed fibers are then given a conventional alkaline scouring treatment in an aqueous detergent or soap solution, rinsed and dried.

From the foregoing description, it is apparent that the present invention provides a satisfactory method for dyeing stereoregular polypropylene fibers with vat dyes. The method of this invention provides level dyeings over a complete range of colors which dyeings have excellent wash fastness, and satisfactory resistance to extraction by dry cleaning solvents and light stability. Moreover, the method of this invention produces satisfactory union dyeing of mixtures of stereoregular polypropylene fibers with cotton fibers, and with regenerated cellulose fibers. Additionally, the method of this invention is readily adaptable to commercial machinery and techniques for package and rope dyeing, and continuous dyeing by padding techniques.

What we claim and desire to protect by Letters Patent is:

1. The process of dyeing fibers consisting essentially of stereoregular polypropylene which comprises:

- (1) applying to said fibers, prior to dyeing, an aqueous solution of a reducing agent for vat dyestuffs, said reducing agent being selected from the group consisting of sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate, and thiourea dioxide, and being effective in neutral and acid solution;
- (2) thereafter contacting the thus pretreated fibers with an acidified aqueous dyebath containing a dye selected from the group consisting of the sulfuric acid esters of leuco vat dyestuffs and a reducing agent for vat dyestuffs as defined in step (1) above;
- (3) dyeing said fibers at the boiling point of the dyebath;
- (4) and subsequently oxidizing the dyed fibers to develop the oxidized form of the dye.

2. The process in accordance with claim 1 wherein the

dye is the sulfuric acid ester of a leuco vat dyestuff of the indigoid type.

3. The process in accordance with claim 1 wherein the reducing agent for vat dyestuff in the pretreatment bath and in the dyebath is sodium formaldehyde sulfoxylate. 5

4. The process for union dyeing a mixture of fibers consisting essentially of stereoregular polypropylene and cotton fibers which comprises:

(1) applying to said fibers, prior to dyeing, an aqueous solution of a reducing agent for vat dyestuffs, said reducing agent being selected from the group consisting of sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate, and thiourea dioxide, and being effective in neutral and acid solution; 10

(2) thereafter contacting the thus pretreated fibers with an acidified aqueous dyebath containing a dye selected from the group consisting of the sulfuric acid esters of leuco vat dyestuffs and a reducing agent for vat dyestuffs as defined in step (1) above; 15

(3) dyeing said fibers at the boiling point of the dyebath; 20

(4) and subsequently oxidizing the dyed fibers to develop the oxidized form of the dye.

5. The process for union dyeing a mixture of fibers consisting essentially of stereoregular polypropylene and regenerated cellulose fibers which comprises: 25

(1) applying to said fibers, prior to dyeing, an aqueous solution of a reducing agent for vat dyestuffs, said reducing agent being selected from the group consist-

ing of sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate, and thiourea dioxide, and being effective in neutral and acid solution;

(2) thereafter contacting the thus pretreated fibers with an acidified aqueous dyebath containing a dye selected from the group consisting of the sulfuric acid esters of leuco vat dyestuffs and a reducing agent for vat dyestuffs as defined in step (1) above;

(3) dyeing said fibers at the boiling point of the dyebath;

(4) and subsequently oxidizing the dyed fibers to develop the oxidized form of the dye.

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