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2,746,836

PROCESS OF DYEING ACRYLONITRILE FIBERS

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9 Claims. (Cl. 8—55)

The present invention relates to improvements in the art of dyeing textile materials comprising acrylonitrile homopolymers and/or heteropolymers containing combined acrylonitrile.

Textile materials composed of acrylonitrile homopolymers or heteropolymers containing combined acrylonitrile are exceedingly difficult to dye with conventional dyestuffs. For example, they are barely tinted with direct cotton dyestuffs. It has been proposed heretofore to dye such textile materials with special dyestuffs. However, the dyestuffs heretofore proposed are quite expensive and increase the cost of processing the textile materials considerably above the processing costs of conventional natural fibers which are dyed readily with inexpensive dyestuffs. The direct cotton dyes are among the most inexpensive dyestuffs but it has not been possible heretofore to use such dyestuffs per se on textiles composed of homopolymers and heteropolymers of acrylonitrile since the depth of the dye shade produced is unsatisfactory for commercial purposes.

It is one object of this invention to provide processes for dyeing textile materials composed partly or wholly of homopolymers of acrylonitrile and/or heteropolymers containing combined acrylonitrile with direct cotton dyestuffs.

It is a further object of this invention to provide processes for dyeing textile materials composed partly or wholly of homopolymers of acrylonitrile and/or heteropolymers containing combined acrylonitrile with direct cotton dyestuffs to obtain a materially deeper dye shade on such textile materials than has been possible heretofore in the use of direct cotton dyestuffs per se.

It is a further object of this invention to provide a textile material composed partly or wholly of homopolymers of acrylonitrile and/or heteropolymers containing combined acrylonitrile dyed with direct cotton dyes, and which has a satisfactory depth of dye shade.

Still further objects and advantages of this invention will appear in the following description and the appended claims.

The processes of this invention are carried out, in general, by immersing a textile material composed wholly or partly of homopolymers of acrylonitrile and/or heteropolymers containing combined acrylonitrile in an aqueous bath containing a direct cotton dyestuff in the presence of a water-soluble quaternary phosphonium salt until a major proportion of the dyestuff in the bath has exhausted on the textile material, after which the textile material is dried. The dye bath is maintained at an elevated temperature, and preferably at the boil, during the dyeing operation.

The term "textile material" as employed herein and in the appended claims is intended to include unspun fibers, yarns, continuous filaments and fabrics. The present invention is directed to the dyeing of textile materials which contain at least 10% by weight of fiber-forming homopolymers of acrylonitrile and/or heteropolymers

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containing combined acrylonitrile, and is particularly directed to the dyeing of textile materials which contain at least 10% by weight of fiber-forming heteropolymers composed of at least 60% by weight of acrylonitrile and 40% by weight or less of an unsaturated organic compound copolymerizable therewith and having the grouping $\text{CH}_2=\text{C}<$ such as, for example, a vinyl or vinylidene compound. Since fiber-forming heteropolymers containing between about 85% and 99% by weight of acrylonitrile and 15 to 1% by weight of a compound having the grouping $\text{CH}_2=\text{C}<$, such as vinyl or vinylidene compounds, copolymerizable therewith have exceptionally desirable textile properties and are particularly amenable to the dyeing processes of this invention, it is preferred to use textile materials composed of at least 10% by weight of such heteropolymers in the processes of this invention.

The compound having the grouping $\text{CH}_2=\text{C}<$ such as vinyl or vinylidene compounds which are copolymerizable with acrylonitrile to form fiber-forming heteropolymers include styrene, nuclear-substituted styrenes such as the alkyl and chloro nuclear-substituted styrenes, vinyl chloride, vinyl acetate, divinyl benzene, alkyl acrylates such as methyl acrylate and ethyl acrylate, vinyl pyridine, vinyl ethers such as vinyl methyl ether and vinyl butyl ether and the like; alkyl methacrylates such as methyl methacrylate, vinylidene chloride and the like.

A wide variety of textiles may be blended with homopolymers of acrylonitrile and/or heteropolymers containing combined acrylonitrile, in amounts up to 90% by weight to form the textile materials defined above. As examples of such textiles may be mentioned fibers or yarns comprised of natural textiles such as cotton, linen, wool or other animal fibers, or synthetic textiles such as viscose and cuprammonium rayon, cellulose acetate, casein, synthetic fiber-forming polyamides such as polyhexamethylene-adipamide and fiber-forming condensation products of ethylene glycol and terephthalic acid.

In carrying out the processes of this invention, the quaternary phosphonium salt, which is an essential ingredient during the dyeing operation, may be incorporated in the textile materials by adding the salt to the spinning solution from which the staple fibers or filaments of the homopolymers of acrylonitrile or heteropolymers containing combined acrylonitrile are prepared, or by spraying or immersing the textile materials with or in a solution, preferably an aqueous solution, of the quaternary phosphonium salt prior to the dyeing operation, or the quaternary phosphonium salts may be added directly to the aqueous dye bath containing the direct cotton dyestuff. The latter procedure, that is, the procedure of adding the quaternary phosphonium salt to the aqueous dye bath is preferred since it is the simplest procedure and gives the best results.

The amount of the quaternary phosphonium salt used may be varied considerably. In general, the depth of dye shade is increased by increasing the amount of quaternary phosphonium salt employed until the optimum amount of the salt is used after which the depth of dye shade is not improved appreciably. It is usually desirable to employ at least 1.0% by weight of the salt, based on the dry weight of the textile material. However, in some instances it is possible to obtain satisfactory results by using as little as 0.1% by weight of the salt, based on the dry weight of textile materials. There is no limiting factor on the upper limit of the salt except its solubility in water and economical considerations. However, it is usually not necessary to employ more than 15% by weight of the salt, based on the dry weight of the textile material. Best results are obtained by using about 4 to 10% by weight of the quaternary phosphonium salt.

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based on the dry weight of the textile materials and accordingly such amounts are preferred.

The above amounts of the quaternary phosphonium salts are readily incorporated in or on the textile materials prior to the dyeing operation or are incorporated directly in the aqueous dye bath.

The amount of direct cotton dyestuff used in the aqueous dye bath may be varied to some extent depending primarily on the particular dyestuff employed and the depth of dye shade desired. In general, from about 0.5 to 5% by weight of the dyestuff, based on the dry weight of the textile material to be dyed, gives satisfactory results.

As in conventional dyeing practice, it is desirable to employ so-called long baths, that is, between about 20 to 150 parts by weight of the dye bath for each part by weight of textile material. Best results are obtained in most instances by using from about 30 to 70 parts by weight of dye bath for each part by weight of textile materials.

The aqueous dye bath may contain the customary dye bath additives such as alkali metal salts, for example, sodium sulfate or sodium chloride to assist in the exhausting the dyestuffs on the textile material, and anion active surface agents to assist in the dyeing operation.

To facilitate the exhaustion of the dyestuff on the textile material it is desirable to maintain the dye bath at an elevated temperature during the dyeing operation. In general satisfactory results are obtained by maintaining the dye bath at a temperature above 70° C. However, the dyeing proceeds much more rapidly at the boiling point of the dye bath and accordingly it is preferred to carry out the dyeing operation at the boil. The dyeing operation is usually completed in from 15 to 60 minutes depending on the operating conditions employed, and the concentrations of quaternary phosphonium salt and dyestuff used, although longer periods may be used.

After a major portion of the dyestuff has exhausted on the textile material or the desired depth of dye shade is attained, the dye bath is cooled and the textile material is then rinsed with water and dried at conventional drying temperatures.

By carrying out the dyeing processes described herein, it is possible to dye textile materials composed of at least 10% by weight of fiber-forming homopolymers of acrylonitrile or heteropolymers containing more than 60% combined acrylonitrile evenly and uniformly with direct cotton dyestuffs to provide textile materials having deep dye shades. Moreover, it is possible in some instances to completely exhaust the dyestuff from the dye bath.

A further understanding of the processes described herein will be obtained from the following specific examples which are intended to be illustrative of this invention, but not limitative of the scope thereof, parts and percentages being by weight unless otherwise specified.

Example I

Five and eight-tenth parts of a yarn composed entirely of staple fibers of a copolymer of 90% of acrylonitrile and 10% of vinyl chloride were immersed in 290 parts of an aqueous bath containing 20% of sodium sulfate, 2% of Stilbene Yellow G (Colour Index Number 620), based on the dry weight of the yarn, and 8% of benzyl tris (dimethylamino) phosphonium bromide, based on the dry weight of the yarns. The dye bath was brought to a boil within a period of 10 minutes and then maintained at the boil for a period of 30 minutes, after which it was cooled for 15 minutes. The yarn was next removed from the bath, rinsed in water and then dried at a temperature of 60° C.

The dyed yarn had a satisfactory dye shade, whereas an equivalent yarn dyed in the same manner but without the use of the phosphonium salt was barely tinted during the dyeing operation and had an unsatisfactory dye shade.

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Example II

Ten parts of a fabric containing yarns composed of 10% wool fibers and 90% staple fibers of a copolymer of 95% acrylonitrile and 5% vinyl pyridine were immersed in 600 parts of an aqueous bath containing 20% of sodium sulfate, 3% of chlorantine Fast Red (Colour Index Number 278), based on the dry weight of the fabric, and 5% of 4-bromobenzyl tris (diethylamino) phosphonium chloride, based on the dry weight of the fabric. The dye bath was brought to a boil within a period of 10 minutes and then maintained at the boil for a period of 45 minutes, after which it was cooled for 20 minutes. The fabric was then removed from the bath, rinsed with water and squeezed to remove excess water. The fabric was next dried at a temperature of 60° C.

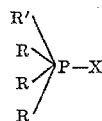
The resulting fabric was dyed evenly and had a satisfactory dye shade, whereas an equivalent fabric dyed in the same manner but without the use of the phosphonium salt was merely tinted and did not have a satisfactory dye shade.

Example III

Ten parts of staple fibers consisting of 8 parts of staple fibers of a copolymer of 95% acrylonitrile and 5% styrene and 2 parts of viscose rayon staple fibers were immersed in 400 parts of an aqueous bath containing 20% sodium sulfate, 4% of chlorantine Fast Blue 4 GL (Colour Index Number 533), based on the dry weight of the fibers, and 10% of benzyl tris (di-isopropylamino) phosphonium bromide, based on the dry weight of the fibers. The bath was brought to a boil within a period of 15 minutes and maintained at the boil for a period of 40 minutes, after which it was cooled for 20 minutes. The fibers were then removed from the bath, rinsed with water and finally dried at 70° C.

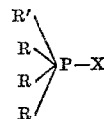
The resulting fibers were evenly dyed and had a satisfactory depth of dye shade, whereas the acrylonitrile fibers in an equivalent fiber mixture which had been dyed in the same manner but without the phosphonium salt were merely tinted and did not have a satisfactory depth of dye shade.

A wide variety of quaternary phosphonium salts are useful in the processes of this invention including compounds having the general formula



where R represents an alkyl group containing from 1 to 4 carbon atoms, R' represents an alkyl group containing from 6 to 20 carbon atoms and where X is a bromine, chlorine or iodine atom. As examples of such compounds may be mentioned decyl trimethyl phosphonium iodide, bromide or chloride, dodecyl, trimethyl phosphonium iodide, bromide or chloride, decyl trimethyl phosphonium bromide or chloride and the like.

Another class of quaternary phosphonium salts which are useful include compounds having the general formula:

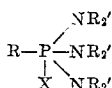


where R is an alkyl group containing from 1 to 4 carbon atoms, R' is an aryl-alkyl radical and X is a bromine, chlorine or iodine atom. As examples of such compounds may be mentioned benzyl trimethyl phosphonium chloride or bromide, benzyl triethyl phosphonium chloride, bromide or iodide and the like.

Still another class of quaternary phosphonium salts which are suitable in the processes of this invention are

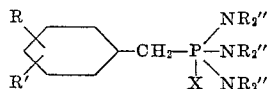
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nitrogen containing quaternary phosphonium salts, particularly compounds having the general formula:



where R is an alkyl group containing from 6 to 22 carbon atoms, R' is an alkyl group containing from 1 to 4 carbon atoms and X is a chlorine or bromine atom. This class of compounds, which may be designated alkyl tris (dialkylamino) phosphonium chlorides or bromides, include such compounds as n-hexyl tris (dipropylamino) phosphonium bromide or chloride, n-heptyl tris (dimethylamino) phosphonium chloride or bromide, n-dodecyl tris (diethylamino) phosphonium chloride or bromide and the like. Such compounds are obtained, in general, by reacting an alkyl bromide or chloride containing from 6 to 22 carbon atoms with a hexa-alkyl phosphorous triamide having the formula: $\text{P}(\text{NR}_2')_3$ where R' has the significance described above, the reaction being carried out at a temperature between about 80 and 250° C. until the corresponding phosphonium halide is formed. Further examples of such halides and methods of preparing these compounds are given in the co-pending application Serial No. 239,175 of William T. Dye, Jr., filed July 28, 1951.

A preferred class of quaternary phosphonium salts for use in the processes of this invention are the nitrogen containing phosphonium halides having the general formula:



where R and R' are chlorine, bromine and hydrogen atoms or alkyl radicals containing from 1 to 5 carbon atoms, R'' represents an alkyl radical containing from 1 to 4 carbon atoms and X is a chlorine or bromine atom. As examples of such compounds may be mentioned benzyl tris (dimethylamino) phosphonium chloride or bromide, 2-chlorobenzyl tris (di-isopropylamino) phosphonium chloride or bromide, 3-bromobenzyl tris (diethylamino) phosphonium chloride or bromide, 4-ethylbenzyl tris (diethylamino) phosphonium chloride or bromide and the like. This class of compounds are prepared, in general, by reacting the corresponding benzyl halide with a hexalkylphosphorous triamide in which the alkyl groups contain from 1 to 4 carbon atoms, the reaction being carried out at normal or elevated temperatures in the presence or absence of solvents or diluents. Further examples of this class of compounds and methods for preparing such compounds are given in the co-pending application Serial No. 223,449 of William T. Dye, Jr., filed April 27, 1951, and the continuation-in-part application Serial No. 278,757, filed March 26, 1952, now U. S. Patent No. 2,703,814.

A wide variety of direct cotton dyestuffs may be used, in addition to those described in the examples, to dye the textile materials hereinbefore referred to in accordance with the processes of this invention. Suitable direct dyestuffs are listed below:

Name of dyestuff	Color Index Number
Amanil Blue 2G.....	406
Amanil Fast Scarlet B.....	382
Soldantine Blue R.....	319
Vegentine Fast Brown B.....	561
Pyrazol Fast Brilliant Blue A.....	319
Trisulfon Garnet BR.....	375
Interchem Direct Brown CN.....	596
Fastusol Red 4 BA-CF.....	278
Pontamine Black BCN.....	581
Diphenyl Dark Green BN.....	583
Pontamine Brown BCW.....	561
Direct Blue 3B.....	477
Direct Violet 3R.....	385

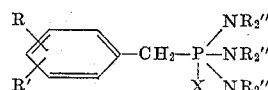
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Other direct cotton dyestuff may be used in the processes of this invention as will be apparent to those skilled in the art.

Various modifications and changes may be made in the processes and dyed textile materials described herein as will be apparent to those skilled in the art to which this invention appertains without departing from the spirit and intent of the invention described herein. It is to be understood therefore that it is not intended to limit this invention except by the scope of the appended claims.

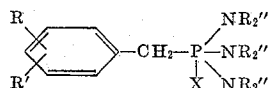
What is claimed is:

1. A dyeing process which comprises immersing textile materials composed of at least 10% by weight of a fiber-forming hydrophobic heteropolymer containing at least 60% by weight of acrylonitrile and not more than 40% by weight of a compound copolymerizable therewith having the grouping $\text{CH}_2=\text{C}$, and containing a water-soluble benzyl tris (dialkylamino) phosphonium halide having the general formula:



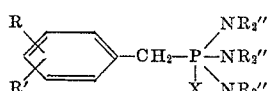
wherein R and R' are selected from the group consisting of chlorine, bromine, and hydrogen atoms and alkyl radicals containing from 1 to 5 carbon atoms, R'' is an alkyl radical containing from 1 to 4 carbon atoms, and X is selected from the group consisting of chlorine and bromine, in an aqueous bath containing a direct cotton dyestuff, raising the temperature of the dye bath above 70° C., maintaining the textile materials in contact with the bath at a temperature above 70° C. until the textile materials are dyed, and thereafter rinsing and drying said materials.

2. A dyeing process which comprises immersing textile materials composed of at least 10% by weight of a fiber-forming hydrophobic heteropolymer containing at least 60% by weight of acrylonitrile and not more than 40% by weight of a compound copolymerizable therewith having the grouping $\text{CH}_2=\text{C}$, in an aqueous solution of a water-soluble benzyl tris (dialkylamino) phosphonium halide having the general formula:



wherein R and R' are selected from the group consisting of chlorine, bromine, and hydrogen atoms and alkyl radicals containing from 1 to 5 carbon atoms, R'' is an alkyl radical containing from 1 to 4 carbon atoms, and X is selected from the group consisting of chlorine and bromine, thereafter immersing said textile materials in an aqueous bath containing a direct cotton dyestuff, raising the temperature of the dye bath above 70° C., maintaining the textile materials in contact with the bath at a temperature above 70° C. until the materials are dyed and then rinsing and drying said materials.

3. A process of dyeing textile materials composed of at least 10% by weight of a fiber-forming hydrophobic substance selected from the group consisting of homopolymers of acrylonitrile and heteropolymers of at least 60% by weight of acrylonitrile and not more than 40% by weight of a compound copolymerizable therewith and having the grouping $\text{CH}_2=\text{C}$, which comprises immersing said textile materials in an aqueous bath containing a direct cotton dyestuff and in the presence of 0.1 to 15% by weight, based on the dry weight of said textile materials, of a water-soluble benzyl tris (dialkylamino) phosphonium halide having the general formula:



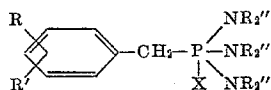
wherein R and R' are selected from the group consisting

of chlorine, bromine, and hydrogen atoms and alkyl radicals containing from 1 to 5 carbon atoms, R'' is an alkyl radical containing from 1 to 4 carbon atoms, and X is selected from the group consisting of chlorine and bromine, raising the temperature of the bath above 70° C., maintaining the textile materials in contact with said bath at a temperature above 70° C. until the materials are dyed and thereafter removing the textile materials from the bath and rinsing and drying said materials.

4. A process according to claim 3, but further characterized in that the benzyl tris(dialkylamino) phosphonium halide is benzyl tris(dimethylamino) phosphonium chloride.

5. A process according to claim 3, but further characterized in that the benzyl tris(dialkylamino) phosphonium halide is benzyl tris(dimethylamino) phosphonium bromide.

6. A process of dyeing textile materials composed of at least 10% by weight of a fiber-forming hydrophobic heteropolymer of at least 60% by weight of acrylonitrile and not more than 40% by weight of a compound copolymerizable therewith having the grouping $\text{CH}_2=\text{C}<$, which comprises immersing said textile materials in an aqueous bath containing a direct cotton dyestuff and from 0.5 to 15% by weight, based on the dry weight of said textile materials, of a water-soluble benzyl tris(dialkylamino) phosphonium halide having the general formula:



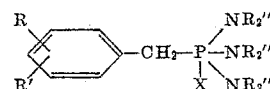
wherein R and R' are selected from the group consisting of chlorine, bromine, and hydrogen atoms and alkyl radicals containing from 1 to 5 carbon atoms, R'' is an alkyl radical containing from 1 to 4 carbon atoms, and X is selected from the group consisting of chlorine and bromine, the weight ratio of bath to textile materials being between 20:1 and 150:1, raising the temperature of the bath to its boiling point, maintaining the bath at its boiling point until the textile materials are dyed, cooling the bath, removing the textile materials from the bath, rinsing the textile materials and then drying the textile materials.

7. A process according to claim 6, but further characterized in that the benzyl tris(dialkylamino) phos-

phonium halide is benzyl tris(dimethylamino) phosphonium chloride.

8. A process according to claim 6, but further characterized in that the benzyl tris(dialkylamino) phosphonium halide is benzyl tris(dimethylamino) phosphonium bromide.

9. A process of dyeing textile materials of at least 10% by weight of a hydrophobic heteropolymer containing between about 85% and 99% by weight of acrylonitrile and about 15 to 1% by weight of a compound having the grouping $\text{CH}_2=\text{C}<$ which comprises immersing said textile materials in an aqueous bath containing a direct cotton dyestuff and in the presence of 0.1 to 15% by weight, based on the dry weight of said textile materials, of a water-soluble benzyl tris(dialkylamino) phosphonium halide having the general formula:



wherein R and R' are selected from the group consisting of chlorine, bromine, and hydrogen atoms and alkyl radicals containing from 1 to 5 carbon atoms, R'' is an alkyl radical containing from 1 to 4 carbon atoms, and X is selected from the group consisting of chlorine and bromine, raising the temperature of the bath above 70° C., maintaining the textile materials in contact with said bath at a temperature above 70° C. until said textile materials are dyed and thereafter removing the textile materials from the bath and rinsing and drying said materials.

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