United States Patent [19]

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[11] **3,709,656**

[45] **Jan. 9, 1973**

[54] **PROCESS FOR DYEING AND FINISHING FIBROUS MATERIAL**

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[22] Filed: **May 19, 1970**

[21] Appl. No.: **38,904**

[30] **Foreign Application Priority Data**

Dec. 30, 1969 Japan 45/1761

[52] **U.S. Cl.**.....**8/17**, 8/174, 8/DIG. 1, 260/46.5 R, 260/46.5 E, 260/825

[51] **Int. Cl.**.....**D06p 5/00**, D06p 7/00

[58] **Field of Search**.....8/DIG. 1, 17, 174; 260/824

[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

A solvent dye solution which comprises a suitable dye in an organic solvent and a polymer or polymerizable monomer of a silicon compound.

6 Claims, No Drawings

PROCESS FOR DYEING AND FINISHING FIBROUS MATERIAL

BACKGROUND OF THE INVENTION

1. Field Of The Invention

This invention relates to a process for solvent-dyeing and finishing fibrous materials, such as yarns, knitted or woven fabrics of synthetic fibers such as nylon, polyester, polyacrylic or polypropylene, or natural fibers such as cotton or wool, or artificial fibers such as rayon or cellulose acetate.

2. Description Of Prior Art

It is known to dye fibrous materials by heating the fibers in an aqueous dye solution or dye dispersion for an extended period of time in order to cause the dye to penetrate into the fiber. If necessary, the dye is mordanted or vat-treated so as to fix the dye into the fiber or to react the dye with the fiber. Although the prior art has expended some considerable effort in an attempt to accelerate the penetration of the dye into the fiber by use of various additives and swelling agents, none of these prior art techniques have been found to be entirely successful for treating the fibers from an aqueous dye solution or for fixing the dye into the fiber from an aqueous dye solution. Many of these prior art processes tend to deleteriously affect the feel of the fiber or undesirably weaken the fiber. They may also cause a low friction resistance, or may be the cause of excessive wrinkling or creasing of the ultimate fabric. Also, it has been found that yarns dyed by state of the art techniques are subject to a high instance of yarn cuts and high friction during knitting or weaving.

For example, in order to shorten the dye time, a thermosole dyeing process has been suggested which comprises heating the fiber with the dye solution at a temperature of more than 140°C. This process, however, has the disadvantage of severely weakening the fiber. It has also been suggested to swell the fiber by use of a carrier, or by use of a solvent containing dye bath. Alternatively, it has been suggested to completely dissolve the dye in the bath. However, each of these techniques suffer the disadvantages of being incapable of dyeing the fibers in a uniform manner and of considerably weakening the fibers.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for dyeing and finishing of fibers which is rapid and will result in a uniform dye deposition.

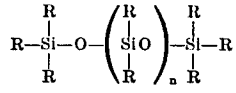
It is a further object of this invention to provide a process for dyeing which will yield a fiber characterized by a low surface friction.

Another object of this invention is to provide a process for dyeing and finishing of fibers which provide a fiber which is characterized by excellent smoothness and softness and which is water-repellent.

A still further object of this invention is to provide a fabric from stretchable yarns which is characterized by outstanding shape-fitting properties.

These and other objects have now herein been attained by the process of dyeing and finishing a fibrous material in a dye bath containing an organic solvent and containing a polymerizable monomer or polymer of silicon.

The polymerizable monomer or polymer of silicon used in this invention can be one of various types of organosilicons. Suitable organosilicons include those having the general formula:

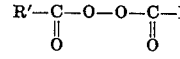


or H

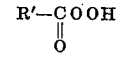
wherein $10<n<10^4$, preferably $10^2<n<3\times10^3$

R is an alkyl radical (methyl, ethyl, butyl, t-butyl, etc.);
an alkenyl radical (vinyl, aryl, hexenyl, etc.);
a cycloaliphatic hydrocarbon radical (cyclohexyl, cyclopentyl, etc.);
an alkylaryl radical (benzyl, β-phenylethyl, etc.); or,
an aryl radical (phenyl, toluyl, xylyl, naphthyl, etc.).

The dye bath solution can also contain a catalyst for bridging the organosilicon such as butyl peroxide, azobis isobutylonitrile and a peroxide such as organoperoxide, or a peroxy acid having the general formula:

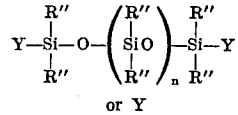


or



wherein R′ represents an alkyl radical (methyl, ethyl, t-butyl, etc.); an alkylaryl radical (benzyl, phenylethyl, etc); or an aryl radical (phenyl, toluyl, chlorophenyl, etc.).

More preferably, it is desirable to use a polyorganosiloxane having the following general formula as the organosilicon:



or Y

wherein Y represents OH or Cl, and numbers of Y are at least 2 and Y/R″ is less than 0.1, *n* is an integer of more than 5, preferably 100 – 3,000; R″ represents an alkyl radical, alkenyl radical, cycloaliphatic hydrocarbon radical, alkylaryl radical, or an aryl radical. Compounds of this type are disclosed in applicant's copending application Ser. No. 855,044, filed Sept. 3, 1969 now U.S. Pat. No. 3,632,423, which discloses the utility of these compounds for imparting shape-fitting properties to garments.

When using the polyorganosiloxane, it is preferable to add one of the following monomer or prepolymer catalysts to the dye bath.

When Y in the polyorganosiloxane is OH, suitable monomer catalysts include those having the general formula:

$$R''' - Si - Z_3$$

wherein R‴ is the same as R″ is selected from the group of alkyl radicals, alkenyl radicals, cycloaliphatic hydrocarbon radicals alkylaryl radicals, and aryl radi-

cals; Z is selected from the group of methoxy, ethoxy, propoxy, isocpropoxy, butoxy, 1-butoxy or acetoxy radicals; suitable prepolymer catalysts include the prepolymers formed from up to 5 moles of the monomer catalyst.

When Y in the polyorganosiloxane is Cl, suitable monomer catalysts include those having the general formula:

$$R'''_2C=NOH$$

wherein R''' has the same meaning as stated above; suitable prepolymer catalysts include prepolymers formed from up to 5 moles of the monomer catalyst. An accelerant can be added to the dye bath, such as dibutyl-tin diacetate, dibutyl zinc diacetate, dibutyl lead diacetate, or the corresponding carbonates or amines. At least a portion of the organosilicon compound may be added to the dye bath using an organic solvent. The particular organic solvent used in this invention is selected depending upon the particular dye, the particular organosilicon, and the fibers being treated.

The following lower aliphatic chlorinated hydrocarbon solvents are especially suitable for use in the solvent dyeing process: chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, perchloroethylene, and tetrachloroethane.

Solubility	g/e 25° C.		
Solvent	Color Ind. Disperse Red 86	Color Ind. Disperse Yellow 65	Color Ind. Disperse Red 32
Water	0.0016	0.004	
ethanol	0.165	0.017	
acetic acid	1.440	0.175	
EG monoethyl ether dimethyl acetoamide	29.96		200
tetrachloroethylene	0.21	0.45	
trichloroethylene	4.42	1.18	
dichloromethane	20.5	73.15	

In many instances, an admixture of various solvents can be used where an acidic dye is being used, such as acidic mordant dyes or reaction type dyes, a solvent mixture containing acetic acid can be used. Suitable solvents include the chloride type solvents, such as trichloroethylene, perchloroethylene, carbon tetrachloride; the fluoride type solvents, such as trichlorofluoromethane, tetrachlorodifluoroethane, trichlorotrifluoroethane; and, the hydrocarbon type solvents such as petroleum ether, benzene, toluene, and xylene. It is not desirable to use the alcohol type solvents or the ester type solvents.

Although water insoluble dyes such as dispersion type dyes are soluble in the above-mentioned solvents, nevertheless, it is preferable to carefully select the dye accelerant used since the solubility of the dye will be decreased by the presence of hydrophilic additives. In preparing the dye bath of this invention, therefore, both the dye and the organosilicon are dissolved in the organic solvent.

The concentration of the dye and the organosilicon, and the ratio of the solvents where a mixture of solvents is used, and the ratio of the acetic acid where an acidic dye is used, are selected depending upon the particular fiber being treated and the process conditions under which the fibers are treated.

In order to increase the solubility of the dyes in perchloroethylene, the following additives are effective: dimethylsulfoxide, dimethylacetamide, and hexamethylphosphoric triamide. In order to prevent dehydration of the fibers when using perchloroethylene, the following additives are effective: alkylarylsulfonate, sorbitan ester of fatty acid, ethoxylated alkylphenol, alkanol amide, and organic phosphates.

A large variety of dyes can be used in this invention with good results. For example, suitable dyes include the acidic dyes, e.g., Benzyl Fast (Ciba), Kayarol (Nippon Kayaku), Suminol Cyanin (Sumitomo Chem.); acidic mordant dyes, e.g., Alizarine Chrome (Mitsui Chem.), Synchromate (Ciba); basic dyes, e.g.,Aizen (Hodogaya), Astra (Bayer; vat dyes, e.g. Fenidon(Geigy), Cibanone (Ciba), Carbon (Nippon Kayaku); reaction type dyes, e.g., Cibacon (Ciba), Micacion (Mitsubishi Chem.), Remalan (Hoechest); dispersion type dyes, e.g., Acetamine (Du Pont), Solaset(ICI); acidic dyes for nylon, e.g., Iraganyl (Geigy), Neonyl (Ciba, Telon, Telon Fast (Bayer); dispersion dyes, e.g., multamine (ICI), Perliton (BASF); reaction type dispersion dyes, e.g., Prociyl (ICI); cationic dyes for acryl fiber, e.g., Aizen Cathilon (Hodogaya), Diacryl (Mitsubishi Chem.); amonionic dyes, e.g., Roracyl(Du Pont); dispersion dyes for polyester fibers, e.g., Dianix (Mitsubishi), Latyl (Du Pont); and azoic dyes, e.g., Teryl Diazo (Meisei).

Where the fiber such as cotton, rayon, nylon, etc., is dyed with an acidic dye, the dye bath is prepared by dissolving the acidic dye, mordant acidic dye or reactive acidic dye in acetic acid and then, if necessary, adding to the mixture a chloride type solvent, a fluoride type solvent, or a hydrocarbon type solvent. The organosilicon is then added to the solution. If mordant treatment is necessary, a solvent type mordant is preferable.

When the fiber is to be dyed with a basic dye bath by a solvent dyeing technique, the dye bath of this invention can be prepared by dissolving the basic dye in an amine type solvent and mixing with a chloride type, hydrocarbon type of fluoride type solvent. The organosilicon compound is then added to the solution.

Water insoluble dispersing dyes, reactive type dispersing dyes, or water insoluble azo dyes are suitable as dyes for solvent dyeing. The dye bath of this invention can be prepared by dissolving the dye in a chloride type, fluoride type or hydrocarbon type solvent and then adding the organosilicon compound thereto. The concentration of dye is preferably less than 10 percent, and usually less than 3 percent. The organic solvent for dissolving a dye should be selected so as to avoid decomposition of the organosilicon, and should be used in an amount sufficient to dissolve the dye. Where cotton or rayon is dyed, a solvent having a substantial amount of acetic acid can be used. The concentration of the organosilicon should be no more than 2 percent, and preferably no more than 0.5 percent.

Where the fibrous material is continuously treated using a high speed process, it is preferable to use high concentrations of dye and organosilicon in the dye bath and to heat the fiber to a relatively high temperature after dipping it in the dye bath.

A wide variety of additives can be added to the dye bath, for example, for the purpose of promoting the penetration of the dye into the fiber or to promote the reactivity of dye at high temperature. It is preferable, however, that the additive be essentially non-reactive to the organosilicon at least at room temperature.

Various types of fibrous materials can be treated by the methods of this invention. For example, good results are obtainable with knitted, woven, twisted, or nontwisted yarns, textured yarns, especially crimped yarns or conjugate stretchable yarns formed from two types of nylon or polyacrylic resins, synthetic fibers, artificial fibers or natural fibers.

The process of the present invention is especially advantageous for imparting excellent shape-fitting properties to crimped yarns or knitted or woven fabrics made from crimped yarns and especially ladies hosiery and panty stockings. The techniques of the present invention provide uniform dyeing and excellent hand characteristics so that a fibrous material or uniform color, good water-repellency and good soil resistance can be obtained by this invention.

Having now generally described this invention, the following examples are provided for purposes of illustration only and are not intended to be limiting in any manner.

EXAMPLE 1

A crimped yarn of $15^d \times 2^f$ of conjugate filament yarn made of nylon 6 and nylon 6.6 is immersed in a bath of 80°C. for 10 minutes, and is treated by a centrifugal separator and dried at room temperature. The bath is prepared by dissolving Elanyl (Ciba) acidic dye in acetic acid to produce a 3 percent solution, and diluting it with a solvent mixture of 25 percent acetic acid and 75 percent perchloroethylene. A mixture of 85 percent polydimethylsilanol, 10 percent methyltriacetylsilane and 5 percent dibutyl tin-diacetate is added to make 0.2 percent of the mixture in the solution.

The dyed crimped yarn obtained is uniformly colored and is characterized by quite low friction. No difficulty was encountered in knitting the unoiled yarn by a seamless hosiery machine. The knitted fabric is characterized by good shape fitness and body garments prepared from this fabric cling snugly with uniform pressure to the body without wrinkling. Fabrics knitted with yarns impregnated with the bath solution which had been heated at 100°C. for 3 minutes, or which have been immersed in the bath solution at 60°C. for 30 minutes, and are mangled with a centrifugal separator and dried, also are characterized by uniform color, low friction and excellent shape fitting properties.

EXAMPLE 2

1. A bath is prepared by dissolving Samalon (Hoechst) in a solvent mixture of 95 percent perchloroethylene and 5 percent acetic acid to make a 2 percent dye solution. A mixture of 90 percent polydimethylsilanol and 10 percent metatriacetoxysilane was added to make 0.2 percent of silicon compound in the bath.

2. A bath is prepared by dissolving Procinyl (ICI) (reacting type dispersing dye) in trichloroethylene to make a 2 percent solution. A mixture of 85 percent polydimethylsilanol and 15 percent triacetoxyvinylsilane was added to make 0.2 percent of silicon compound in the solution.

3. A bath is prepared by dissolving Elanyl (Ciba) in acetic acid to make a 10 percent dye solution. This solution is diluted with perchloroethylene to make a solution of 2 percent dye, 8 percent acetic acid, and 90 percent perchloroethylene. A mixture of 99 percent polymethylvinylsiloxane and 1 percent lauryl peroxide is added to make 0.2 percent of silicon compound in the bath.

Each filament yarn of nylon 6 having $15^d \times 2^f$ is immersed in the bath at 80°C. for 30 minutes and mangled and dried, respectively. Remarkably uniform color dyeing and low friction is found in each case.

Each yarn obtained is twisted either 200 T/M right turns or 200 T/M left turns, respectively. Ladies' panty stockings knitted from the yarns of right twist and left twist in alternative courses were prepared and these showed excellent shape fitting properties and excellent soil resistance.

EXAMPLE 3

A fabric knitted with polyethylene teraphthalate crimped yarns made by a false twisting-heat setting treatment is treated with the following bath.

The bath is prepared by dissolving Dianix (Mitsubishi Chem.) (dispersing dye) in a mixture of 50 percent trichloroethylene and 50 percent perchloroethylene to make a 2 percent dye solution. A mixture of 90 percent phenylmethylsilanol and 10 percent methyltriacetoxysilane is added to make 0.2 percent of silicon compound in the bath.

The knitted fabric is immersed in the bath at 60° C. for 20 minutes and mangled and dried at 80° C. for 10 minutes. Remarkably uniform dyeing effect is obtained by the process and the product is characterized by excellent properties.

EXAMPLE 4

A fabric for carpet woven with polyacrylonitrile staple fibers is treated with the following bath.

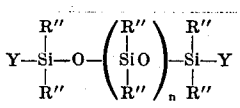
The bath is prepared by dissolving Diacryl (Mitsubishi Chem.) in a mixture of 3 percent acetic acid, 5 percent formalic acid, and 92 percent trichloroethylene to make 2 percent of dye solution. A mixture of 85 percent polydimethylsilanol and 15 percent triacetoxyvinylsilane is added to make 0.2 percent of silicon compound in the bath. The woven fabric is immersed in the bath at 80° C. for 10 minutes and mangled and dried at 80°C. Remarkably uniform dyeing effect is obtained by the process and the fabric treated has excellent soil resistance. Each fabric dyed by this invention is characterized by less discoloring, excellent uniform dyeing, good soil resistance, and good hand feel, in comparison with fabrics dyed with the same bath in which the silicon compound is not added.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit and scope of the invention.

What is claimed and intended to be covered by letters patent is:

1. A process for solvent dyeing and finishing fibrous material which comprises:

treating a fibrous material in a solvent dye solution prepared by dissolving a soluble dye in an organic solvent and including in said dye solution a silicone compound having the formula:



wherein R'' is Y or a group consisting of an alkyl, alkenyl, cycloaliphatic hydrocarbon, alkylaryl and aryl, Y is OH, and wherein Y/R'' is less than 0.1, *n* is an integer of more than 5, wherein a monomer or polymer compound is included in the dye solution, wherein said monomer compound has the formula:

$$R''' - Si - Z_3$$

wherein R''' is selected from the group consisting of alkyl, alkenyl, cycloaliphatic hydrocarbon, alkylaryl and aryl, and Z is selected from the group consisting of lower alkoxy and acetoxy, and the polymer compound is a polymer of at least 5 moles of said monomer compound.

2. The process of claim **1**, wherein Y is OH and said compound is a monomer compound having the formula:

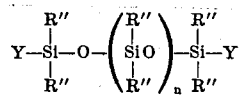
$$R''' - Si - Z_3$$

wherein R''' and Z are as defined above.

3. The process of claim **1**, wherein Y is OH, and said compound is a polymer compound containing at least 5 moles of the monomer compound:

$$R''' - Si - Z_3$$

4. A solvent dye solution which comprises a soluble dye in an organic solvent and a silicone compound having the formula:



wherein R'' is Y or a group consisting of an alkyl, alkenyl, cycloaliphatic hydrocarbon, alkylaryl and aryl, Y is OH, and wherein Y/R'' is less than 0.1, and *n* is an integer of more than 5, wherein a monomer or polymer compound is included in the dye solution, wherein said monomer compound has the formula:

$$R''' - Si - Z_3$$

wherein R''' is selected from the group consisting of alkyl, alkenyl, cycloaliphatic hydrocarbon, alkylaryl and aryl, and Z is selected from the group consisting of lower alkoxy and acetoxy, and the polymer compound is a polymer of at least 5 moles of said monomer compound.

5. The product of claim **4**, wherein Y is OH and said catalyst is a monomer compound having the formula:

$$R''' - Si - Z_3$$

wherein R''' and Z are as defined above.

6. The product of claim **4**, wherein Y is OH, and said compound is a polymer compound containing at least 5 moles of the monomer compound having the formula:

$$R''' - Si - Z_3$$

wherein R''' and Z are as defined above.

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