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3,326,846

USE OF FLUOROALCOHOLS IN THE DYEING OF SYNTHETIC POLYMERS

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5 Claims. (Cl. 260-40)

This application is a continuation-in-part of application Ser. No. 159,163, filed Dec. 13, 1961, which is now abandoned.

This invention relates to a novel process for dyeing synthetic polymers. More particularly it relates to a dyeing process wherein said dye solution contains a fluoroalcohol.

Polymers such as polyesters, polyamides and acrylics are in widespread use as films, fibers, etc. Numerous end-uses of these polymers require that the finished objects made from polyesters, acrylics, polyamides, etc., be colored. Examination of the existing art relating to the dyeing of finished goods manufactured from the above-mentioned polymers reveals that the presently accepted dyeing methods are deficient in a number of respects and improvements in the established dyeing techniques are needed.

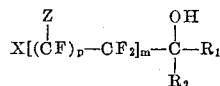
Thus, in dyeing of these polymers, in most instances long dyeing times (generally one hour or more) at high temperatures (100-150° C., or even higher) must be used in order to obtain the desired depth of shade. Dyeing assistants, such as carriers, surfactants, buffers and leveling agents must generally be used in order to obtain satisfactory dyeings in a reasonable time. In many cases, the corresponding dyeing times must be purposely prolonged by the addition of retarders to the dyebath in order to obtain level dyeings. The slow rates of dyeing from aqueous dyebaths can be increased by the use of pressure equipment. Pressure dyeing, however, requires the use of expensive equipment and does not permit continuous dyeing of fabrics and films. The use of additives required in most existing dyeing procedures is frequently objectionable because of the resulting alteration of the properties of the dyed polymers and/or because of the resulting degradation of dye fastness. In many cases post-treatment of the dyed polymers is necessary in order to remove the additives and thereby to restore the original properties of the polymer and to increase the color fastness of the finished product.

An object of this invention is to provide a new process for dyeing synthetic polymeric compositions. Another object is to provide such a process wherein the synthetic polymers are dyed to give level shades much more rapidly and at lower temperatures than the dyeing processes of the prior art. Still another object is to provide such a process wherein the use of harmful additives or of cumbersome procedures is eliminated. A further object is to provide such a process wherein the dyeing exhibits the full fastness properties inherent in the dye utilized and the polymer is not degraded. Yet a further object is to provide such a process which is readily adaptable to a continuous process. Still other objects will be apparent from the following description of the invention.

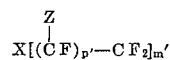
These and other objects are accomplished in accordance with the invention by a process for dyeing a synthetic polymer, e.g., polyester, acid-modified polyethylene terephthalate, acrylic, sulfonate-modified acrylic and nylon polymers, which comprises treating said polymer at 70 to 120° C. for about 1 second to 15 minutes with an aqueous dye solution containing 50 to 99% by weight of water and 1 to 50% by weight of a fluoroalcohol

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vased on the weight of the solution exclusive of the dye, said fluoroalcohol being selected from the group consisting of 2,2,3,3-tetrafluorocyclobutyl methanol, an aliphatic fluoroalcohol compound having a maximum of 8 carbon atoms of the formula

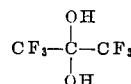


wherein X is a member selected from the group consisting of hydrogen, fluorine and chlorine, Z is a member selected from the group consisting of fluorine and CF₃, p is a number 0 and 1, m is a number of 1 to 6 when p is 0 and a number of 1 to 3 when p is 1, R₁ is a member selected from the group consisting of hydrogen,



and alkyl of 1 to 5 carbon atoms, R₂ is a member selected from the group consisting of hydrogen, hydroxyl and alkyl of 1 to 5 carbon atoms, p' is a number 0 and 1, m' is a number of 1 to 5 when p' is 0 and a number 1 and 2 when p' is 1, and a cycloaliphatic fluoroalcohol compound having a maximum of 8 carbon atoms of the above formula wherein R₁ and R₂ taken together form a ring member of 5 and 6 carbon atoms with their commonly adjoining carbon atom.

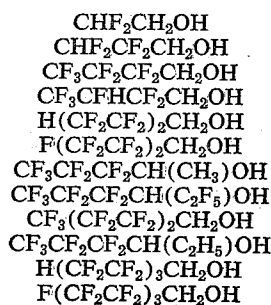
Preferably, the above-defined fluoroalcohol is present in the dye solution in an amount of from 5 to 10% by weight based on the amount of solution. The concentration of the fluoroalcohol within the broad range, however, is dependent upon the solubility of the fluoroalcohol in water. The lower-molecularweight fluoroalcohols, e.g.,

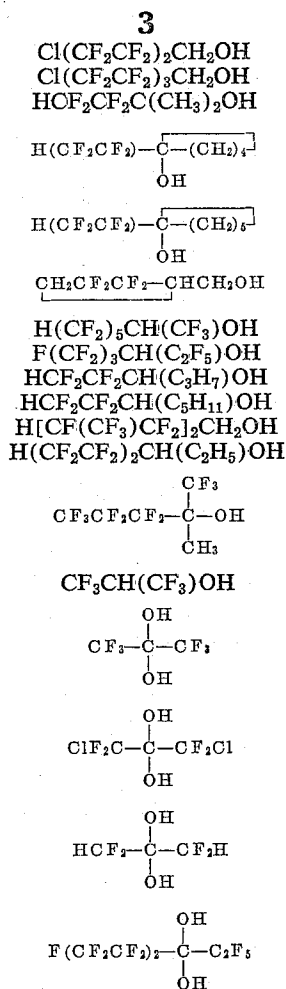


HCF₂CF₂CH₂OH, etc., are in general miscible with water in all proportions, while H(CF₂CF₂)₃CH₂OH is soluble only to the extent of about 1% by weight at the boil. As a practical matter, the amount of fluoroalcohol will usually be between about 1 to 10% by weight of the fluoroalcohol/water mixture. However, as previously pointed out, the solution, if desired, can contain up to 50% by weight of the fluoroalcohol.

The amount of dye employed in the dye bath to give the desired color can vary over a wide range. For example, an amount of about 0.01% by weight of dye based on the total weight of fluoroalcohol and water to that amount which provides a saturated solution of dye in the dye bath is illustrative of the operable range. The amount selected would depend upon various factors familiar to one skilled in the art—tintorial value of dye selected, its solubility in the dye bath, nature of the material to be dyed, depth of shade desired, and mode of dyeing.

Examples of fluoroalcohols useful in this invention include:





The latter four compounds are illustrative of a class of compounds known as fluoroalkyl gemdiols (also known as ketone hydrates). Compounds of this type are prepared by the addition of water to the appropriate ketone.

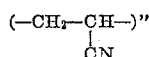
The dyeing procedure comprises immersing a polymer, fiber, fabric or yarn into an aqueous dyebath maintained at a temperature of 70 to 120° C. containing a fluoroalcohol for about 1 to 900 seconds depending upon the depth of shade desired. The procedure is easily adapted to a continuous operation with a short residence time of the polymer, etc., in the dyebath. After treatment in the dyebath, the polymer is removed, rinsed with water, is scoured and is dried.

Polymers, preferably in fiber form, which are dyed advantageously by this invention include:

(1) Polyester polymers defined by R. E. Kirk and D. F. Othmer, in *Encyclopedia of Chemical Technology*, vol. 10, 603, Interscience, New York (1953), as "A high polymer ester containing the recurring structural units, $(-\text{OCH}_2\text{CH}_2\text{OOC}_6\text{H}_4\text{CO}-)$."

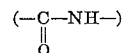
(2) The term "polyester polymers" as used herein also includes acid-modified polyethylene terephthalate polymers containing acidic sites, e.g., metal sulfonate groups, as described more fully in Belgian Patent No. 549,179, granted July 14, 1957 and British Patent No. 826,248, published Dec. 31, 1959.

(3) Acrylic fibers defined by Textile World, "Man-Made Fiber Table, 1959 Revision," McGraw-Hill Publishing Company, Inc., New York (1959), as "A manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile units

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(4) Therefore, the term "acrylonitrile" as used herein also includes sulfonate-modified acrylic polymers such as those described in U.S. Patents 2,837,500 and 2,837,501.

(5) Nylon polymers defined by R. E. Kirk and D. F. Othmer, loc. cit., as "Condensation products which contain recurring amide groups,

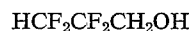


as integral parts of the polymer chains."

This invention will be further illustrated by but is not intended to be limited to the following examples wherein the parts are by weight unless otherwise indicated.

EXAMPLE I

A dyebath is prepared by dissolving in a suitable vessel 1.2 g. of the dye C.I. Basic Blue 4 (C.I. 51004) in 100 ml. by volume of a 50% by weight aqueous solution of



and is brought to the boiling point by immersing the vessel into a preheated oil bath. Samples of two g. each of sulfonate-modified polyester fabric are immersed with agitation into the boiling solution of the dye maintained at 95 to 100° C. for periods of 15 seconds, one minute and five minutes, respectively. At the end of each dyeing period, a sample of fabric is removed from the dyebath, rinsed with water, scoured for five minutes with a solution containing 1,000 ml. of water and one g. of sodium salt of the sulfate of the condensation product of ethylene oxide with oleyl alcohol and is dried. The resultant blue dyeings are level, bright dyeings, the depth of shade increasing with dyeing time.

An acid-modified acrylic fiber substituted in place of the polyester fabric described above in this example gives comparable results except that level dyeings of lighter blue shades are obtained.

Other cationic dyes which can be substituted in place of the above dye that are suitable for dyeing acid-modified polyester and acrylic fibers include: [p-(1-amino-4-hydroxy-2-anthraquinonyloxy)benzyl]triethyl ammonium ethyl sulfate (U.S. Patent 2,888,467), cationic triaryl methane, xanthene, cyanine, thiazole dyes, e.g., as described in U.S. Patent 2,922,690; British patent specification 787,891, or a mixture of two or more thereof. Other compounds which may be employed are anthraquinone compounds having pendant cationic groups, and the cationic dyes described in U.S. Patent 2,821,526, obtained by coupling a diazotized aminophenacyl ammonium salt with an aromatic amine; in U.S. Patent 2,832,764, quaternized derivatives of the reaction product of a nitrogen-containing heterocyclic hydrazine compound with an aromatic phenol, amine, and enol or indole; and in U.S. Patent 2,889,314, cationic dyes from monoazo derivatives of benzothiazole coupled to an aminobenzene compound.

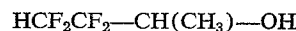
EXAMPLE II

The procedure of Example I is repeated using a dyebath comprising 1% aqueous solution of $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$. Level dyeings of light to medium blue shades on acid-modified polyester fabric are obtained.

An equivalent amount of $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{OH}$ is substituted in this example for $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$, level dyeings of approximately equal depth being obtained.

EXAMPLE III

A dyebath is prepared by dissolving 1.2 g. of the dye C.I. Basic Blue 4 (C.I. 51004) in 100 ml. by volume of a 10% by weight aqueous solution of



Samples of two g. of acid-modified polyester fabric are prescoured for five minutes at about 82° C. with a solution containing 1,000 ml. of water and one g. of the sodium salt of the sulfate of the condensation product

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of ethylene oxide with oleyl alcohol, are washed with water and are dried. The fabric samples are immersed into the dyebath with agitation near the boiling point, i.e., 95 to 100° C. for periods of 15 seconds, one minute and five minutes, respectively. At the end of each dyeing period a sample of fabric is removed from the dyebath, rinsed with water, and scoured for five minutes with the prescouring solution described above. Level, blue dyeings of medium to heavy shades are obtained.

This example is repeated using 10% by weight solutions of $\text{HCF}_2\text{CF}_2\text{CH}_2\text{OH}$, $\text{HCF}_2\text{CF}_2\text{C}(\text{CH}_3)_2\text{OH}$, $\text{H}(\text{CF}_2-\text{CF}_2)_2\text{CH}_2\text{OH}$, and 2,2,3,3-tetrafluorocyclobutyl methanol for a dyeing time of 15 seconds, 1 minute and 5 minutes, respectively. All the dyeings obtained are level, medium to heavy, with rapid build-up.

EXAMPLE IV

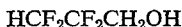
A dyebath is prepared by dissolving 1.2 g. of the dye C.I. Basic Blue 4 (C.I. 51004) in 90 ml. of water. To the bath are added 10 ml. of 1,3-dichloro-1,1,3,3-tetrafluoropropane-2,2-diol. Samples of two g. of acid-modified polyester fabric, prescoured as described in Example III, are immersed in the dyebath with agitation near the boiling point, i.e., 95-100° C., for periods of 30 seconds, one and five minutes. At the end of the dyeing period the fabric is removed, rinsed and scoured as above. Level, medium to heavy dyeings are obtained.

When the amount of fluoroalcohol in the dyebath in above example is change to 1.5 and 20 ml., the dyeing varies from light to very heavy shades. The rate of dyeing increases rapidly with the increase of concentration of the fluoroalcohol.

On replacing the fluoroalcohol of the above example by hexafluoropropane-2,2-diol and hexafluoropropane-2-ol a similar increase in the dyeing rate is observed.

EXAMPLE V

A dyebath is prepared by dispersing 0.9 g. of the blue dye, 1-hydroxy-4-p-anisidinoanthraquinone in 100 ml. by volume of a 10% by weight aqueous solution of



The dyeing procedure of Example I is repeated using fabric samples of unmodified polyethylene terephthalate for dyeing times of 15 seconds, one minute and five minutes, and 15 minutes, respectively. Uniform blue dyeings of light to heavy shades are obtained.

Comparable amounts of the following disperse dyes can be used singly or in combination in place of the 1-hydroxy-4-p-anisidinoanthraquinone described above in this example with uniform dyeings being obtained. The depth of shade, of course, varies with the dyeing time. By "disperse dyes" is meant water-insoluble organic colors which are applied to the fiber from near-colloidal aqueous dispersion.

Blue, monochloro-4,5-diaminochrysazin

Blue, 1,4-diamino-N-(3-methoxypropyl)-2,3-anthraquinonedicarboximide (U. S. P. 2,753,356)

Blue, 1,4-diamino-N-(3-hydroxypropyl)-2,3-anthraquinonedicarboximide (U. S. P. 2,628,963)

Blue, 1,4-diamino-N-(2-hydroxyethyl)-2,3-anthraquinonedicarboximide (U. S. P. 2,628,963)

Violet, 1,4-dianilinoanthraquinone

Violet, 1-anilino-4-hydroxyanthraquinone

Yellow, 3-hydroxyquinophthalone

Red, 1-amino-4-hydroxy-2-phenoxyanthraquinone

Orange, disazo dye obtained by coupling diazotizing aniline to 2,5-dimethoxyaniline, disazotizing the amino azo dye formed and coupling to phenol.

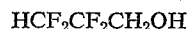
All disperse dyes normally used for dyeing hydrophobic fibers can be used in this invention.

EXAMPLE VI

A dyebath prepared in a suitable vessel by dissolving 1.48 g. of the red azo dye obtained by coupling diazo-

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tized 1-amino-2-hydroxy-4-benzene sulfonamide to beta-naphthol, and forming the half cobalt complex, in 100 ml. by volume of a 10% by weight aqueous solution of



is brought to the boiling point by immersing the vessel into a preheated oil bath. Samples of two g. of nylon yarn are immersed with agitation into the boiling dye bath maintained at 95 to 100° C. for periods of three seconds, 15 seconds, 30 seconds and two minutes, respectively. The yarn is rinsed with water, scoured for five minutes at 82° C. with a solution containing 1,000 ml. of water and one g. of the sodium salt of the sulfate of the condensation product of ethylene oxide with oleyl alcohol, is washed with water and is dried. Level medium to heavy red shade dyeings are obtained.

Comparable amounts of the following dyes may also be used in place of the dye in Example VI, with uniform dyeings being obtained: nitrodiphenylamine dyes as described in U.S. Patents 2,269,147 and 2,422,029; metalized azomethine dyes such as the chromium complex of the azomethine dye obtained from 2-aminophenol-4-sulfonamide and 3,5-dichlorosalicylaldehyde; and other metalized azo dyes, such as the chromium complexes described in U.S. Patents 2,671,081 and 2,885,392.

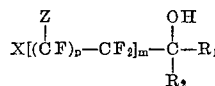
The invention is useful for dyeing the specified synthetic polymers, fibers, fabrics, yarns, etc. The polymers may also be pretreated with a fluoroalcohol (100%) and subsequently dyed rapidly without a carrier.

An advantage of this invention is that the fibers are dyed level shades with exceptional rapidity at comparatively lower temperatures. At the lower temperatures, the possibility of altering the fibers, etc., and decomposing the dyes is avoided. Additional advantages of the process are that the uniform dyeings exhibit good build-up and full fastness properties inherent in the dyes utilized. A further advantage is that by use of a fluoroalcohol the dyes useful in this invention include those which lacked adequate buildup or had insufficient solubility in the aqueous systems. Still further advantages are that the process is readily adaptable to a continuous dyeing process; no additives such as carriers, leveling agents, dispersing agents, etc., have to be added to the dyebath or incorporated in the dye; and there is no carrier removal problem since the fluoroalcohol does not remain on the fiber, etc., and is easily washed out.

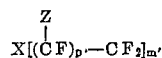
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

I claim:

1. A process for dyeing a synthetic polymer selected from the group consisting of polyester, acrylonitrile, and nylon polymers, which comprises treating said polymer at 70 to 120° C. for up to 15 minutes with an aqueous dye solution containing 50 to 99% by weight of water and 1 to 50% by weight of a fluoroalcohol based on the weight of the solution exclusive of the dye, said fluoroalcohol being selected from the group consisting of 2,2,3,3-tetrafluorocyclobutyl methanol, an aliphatic fluoroalcohol compound having a maximum of 8 carbon atoms of the formula



wherein X is a member selected from the group consisting of hydrogen, fluorine and chlorine, Z is a member selected from the group consisting of fluorine and CF_3 , p is a number 0 and 1, m is a number of 1 to 6 when p is 0 and a number of 1 to 3 when p is 1, R₁ is a member selected from the group consisting of hydrogen,



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and alkyl of 1 to 5 carbon atoms, R_2 is a member selected from the group consisting of hydrogen, hydroxyl and alkyl of 1 to 5 carbon atoms, p' is a number 0 and 1, m' is a number of 1 to 5 when p' is 0 and a number 1 and 2 when p' is 1, and a cycloaliphatic fluoroalcohol compound having a maximum of 8 carbon atoms of the above formula wherein R_1 and R_2 taken together form a ring member of 5 and 6 carbon atoms with their commonly adjoining carbon atom.

2. A process as defined in claim 1 wherein said fluoroalcohol is present in said dye solution in an amount of from 5 to 10% by weight.

3. A process as defined in claim 1 wherein said polymer is an acid-modified polyethylene terephthalate.

4. A process as defined in claim 1 wherein said fluoroalcohol is $HCF_2CF_2CH_2OH$.

5. A process as defined in claim 1 wherein said fluoro-

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alcohol is present in said dye solution in an amount of from 1 to 10% by weight.

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