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CELLULOSE ACETATE FIBERS HAVING WOOL DYEING PROPERTIES AND A SPINNING SOLUTION THEREFOR

John R. Caldwell, Kingsport, Tenn., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

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7 Claims. (Cl. 106—186)

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This invention relates to the manufacture of synthetic fibers from lower fatty esters of cellulose, which fibers are susceptible to dyeing by wool dyestuffs.

In the textile industry it is often desirable to use fibers of different kinds in the manufacture of fabric. After the fabric has been woven, it may then be subjected to a dyeing operation and it is often desirable that the fibers have dyeing properties which are substantially equivalent. In those fabrics in which cellulose ester fibers are combined with the fibers of natural wool, it has commonly been necessary heretofore to employ both an acetate dyestuff and a wool dyestuff to impart color to the fabric. In many cases considerable difficulty has been encountered in matching the shades of the wool fibers and the cellulose ester fibers. In addition, the two types of dyestuffs often respond differently to laundering, light-fading, etc., resulting in fabrics having a spotty or irregular appearance after they have been exposed to conditions of wear.

Many attempts have been made heretofore to impart wool dyeing properties to cellulose ester fibers but the results obtained have not been too satisfactory. The idea commonly held is that the dyeing of wool fibers by acid type dyestuffs takes place through the reaction of the sulfonic acid groups in the dye molecule with amine groups in the wool to form a salt linkage. To impart wool dye affinity to cellulose ester fibers, compounds have been incorporated therein having basic amino groups, resembling those present in natural wool. In most cases heretofore the fibers which have been so prepared would take up only small amounts of dyestuff to give a weak shade, or the dye employed to dye the cellulose ester fibers would show poor stability toward light-fading and laundering.

It is an object of my invention to prepare fibers of lower fatty esters of cellulose having good susceptibility to acid dyes and good stability, when so dyed, to fading by light or by laundering. Other objects of my invention are apparent herein.

I have found that fibers may be prepared from lower fatty acid esters of cellulose bearing a very close resemblance to wool in their behavior toward acid type dyestuffs. I have found that cellulose ester fibers may be prepared which when dyed in the same bath with wool are so colored that the shade produced is a close match for the color on the wool both as to depth and shade. I have found that fabrics made from wool in combination with the lower fatty acid esters of

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cellulose fibers produced in accordance with my invention may be union dyed in an acid type wool dyebath to produce a uniform color, free of spots or irregularities.

In its broadest aspects my invention comprises incorporating in cellulose ester fibers a small proportion of a polymeric amine having the structure:

$$\left(-R'-\underset{\underset{R}{|}}{N}-R'-O-CO-R''-CO-O-\right)_m$$

in which

R is an alkyl radical having 1–4 carbon atoms.

R′ is a hydrocarbon radical having 2–4 carbon atoms and of a structure such that at least two carbon atoms separate the N and O.

R″ is a saturated or unsaturated hydrocarbon radical containing 1–8 carbon atoms.

m is a whole number greater than 6.

I have found that this polymeric material may be incorporated in the cellulose ester fibers either by treatment of the fiber after its formation with a solution of the polymer in an organic solvent or preferably by incorporating the polymer in the cellulose ester fibers by adding it directly to the spinning dope. I have found that the polymer is completely compatible with the cellulose ester so that they form a homogeneous system and that the polymer forms an insoluble complex with the acid dyestuff.

The linear polymeric amines employed in the process of the invention are most conveniently prepared by the interaction of dibasic acids with alkyl-dialkylol amines having the general structure:

$$HO-R'-\underset{\underset{R}{|}}{N}-R'-OH$$

in which R and R′ are radicals as defined heretofore. The polymer is formed by the elimination of water to give a linear polyester containing tertiary amine groups in the main valence chain. The alkyl-dialkylol amines, which are useful in my process, include ethyl diethanol amine, methyl diethanol amine, methyl diisopropanol amine, butyl diethanol amine

$$HO-CH_2-\underset{\underset{CH_3}{|}}{CH}-N-C_2H_4-OH$$
$$\qquad\qquad\qquad\quad\underset{\underset{CH_3}{|}}{}$$

and

$$HO-C_3H_6-N-C_2H_4-OH$$
$$\qquad\qquad\quad\underset{\underset{C_2H_5}{|}}{}$$

In general any dibasic acid containing 3–10 carbon atoms is suitable. The dibasic acid may

be aliphatic or olefinic or it may be an aromatic derivative. Aliphatic dibasic acids which may be employed in preparing the polymeric amines for use in accordance with my invention are malonic acid, succinic acid, glutaric acid, alpha methyl glutaric acid, adipic acid, sebacic acid, and the like. Olefinic dibasic acids which may be employed are represented by maleic acid and fumaric acid. Aromatic dibasic acids which may be employed include phthalic acid, teraphthalic acid, 2-methyl phthalic acid or similar phthalic acid derivatives. Either the free acids, their anhydrides, or their esters may be employed as the starting materials for the reaction with alkyl-dialkylolamine in preparing polymeric amines for use in my invention.

The formation of the polymeric amines by reacting the dibasic acid and alkyl-dialkylol amine may be carried out by heating the reactants under conditions that allow the escape of water. The acid and the amine may be heated in a suitable vessel with agitation either with or without a polymerization catalyst. If desired, the reacting materials may be heated in the presence of an entraining liquid to remove water by azeotropic distillation. Suitable entraining liquids are benzene, toluene, xylene, kerosene, dibutyl ether or the like. The preparation of the polymeric amines may be carried out within the range of 110°–200° C., but it is preferred to use a temperature of 150°–175° C. for this purpose. It is ordinarily desirable to carry out the polymerization reaction to a point where the polymer has an equivalent weight as an acid, of 5,000–10,000 although polymers having equivalent weights above or below this range are often suitable for use in my invention. The course of the reaction may be followed by titration of samples of the reacting mass with standard alkali in alcohol solutions, using phenolphthalein as the indicator.

The most desirable means of preparing cellulose ester fibers in accordance with my invention is by dissolving the polymeric amines in the spinning dope which consists of a solution of the cellulose ester in a volatile solvent. Ordinarily the solvent employed for spinning cellulose ester is acetone, and the polymeric amines may be dissolved therein at the same time as the cellulose ester is dissolved. It is to be understood, however, that other solvents may be employed for spinning cellulose esters, and my invention also includes cases using other solvents in which these polymeric amines are incorporated. To secure good affinity for wool dyes, the cellulose ester fibers should contain 10–30% of the polymeric amine.

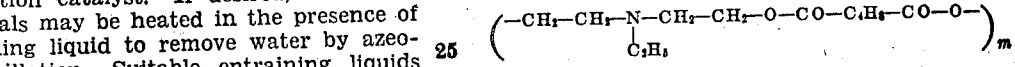
Instead of incorporating the polymeric amines in the spinning dope, it may be applied to the cellulose ester fibers from its solution in an organic solvent such as alcohol or benzene. I have found, however, that a more uniform dispersion of polymer throughout the fiber cross section is obtained in those cases where the polymer is incorporated directly into the spinning dope.

My invention is adapted to impart a wool dyeing property to the various lower fatty ester acids of cellulose which have been employed for preparing synthetic fabrics. For instance, cellulose acetate which has been hydrolyzed to an acetyl content of 39–40% is much employed, especially in acetone solution for making synthetic fibers. Also other cellulose esters such as cellulose acetate propionate or cellulose acetate butyrate having a propionate or butyrate of 1 to 6% such as

described in U. S. Patent No. 2,223,376 of Malm are of interest in this case. Also cellulose esters having an even higher propionate or butyrate content may be employed. My invention applies to the fibers prepared from any of these cellulose esters. By my invention fibers are prepared therefrom which are susceptible to dyeing by any of the wool dyestuffs containing sulfonic acid groups in the dye molecules. The following examples illustrate my invention:

Example I

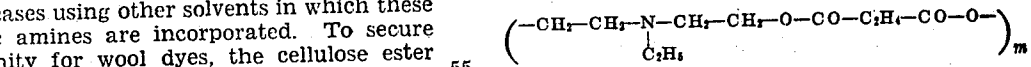
146 grams of adipic acid and 133 grams of N-ethyl diethanolamine were mixed together in an esterification apparatus equipped with a continuous decanter. One hundred cc. of xylene was added and the mixture was refluxed for 8–10 hours. Approximately 35 cc. of water was eliminated. A sample of the polymer dissolved in alcohol and titrated with sodium hydroxide solution showed an equivalent weight of 2,000–3,000. The polymer has the structure:



It was a pale yellow oil, soluble in alcohol, acetone, and benzene. It was insoluble in water, soluble in dilute acids, and thrown out of acid solution by the addition of sodium hydroxide. A spinning dope was prepared having the composition: 25 parts cellulose acetate having an acetyl content of 39%, 4 parts of the polymeric amine and 75 parts of acetone. Fibers were spun from this solution by extruding it through a spinning cabinet under evaporative conditions. The resulting fibers dyed to a dark even shade in the following dye bath: 2 parts LRC Tinting Blue (Color Index No. 671), 100 parts of water, 5 parts of sodium sulfate and 10 parts of acetic acid.

Example II

A mixture was prepared consisting of 133 grams of N-ethyl diethanolamine, 100 grams of succinic anhydride, and 100 cc. xylene. This mixture was heated in an esterification apparatus for 20–24 hours. Approximately 18 cc. of water was eliminated. The xylene was removed under a vacuum to leave a residue of light yellow, viscous oil. The resulting polymer had the structure:



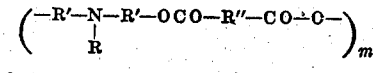
A sample dissolved in alcohol and titrated with standard sodium hydroxide showed an equivalent weight of 10,000–14,000. The polymeric amine formed was soluble in acetone, alcohol, and benzene. It was soluble in dilute acids and may be thrown out of solution by alkali.

A spinning dope was prepared consisting of 25 parts of cellulose acetate, 5 parts of the polymeric amine, and 75 parts of acetone. Yarn was spun from the solution by an evaporative process as referred to in the preceding example. The resulting fiber was found to dye well with LRC Tinting Blue (Color Index No. 671), National Tinting Yellow NCL (Color Index No. 640), National Alkali Fast Green 2G (Color Index No. 735), and Acid Green 2G (Color Index No. 670).

I claim:

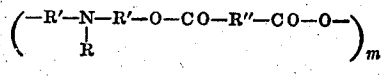
1. Cellulose ester fibers having wool dyeing properties essentially consisting of a lower fatty acid ester of cellulose and approximately 10–30%,

of a polymeric amine which is a viscous oil having the formula:



in which R is an alkyl radical having 1–4 carbon atoms, R′ is a saturated hydrocarbon radical having 2–4 carbon atoms, and of a structure such that at least 2 carbon atoms separate the N and O, R″ is a saturated hydrocarbon radical containing 1–8 carbon atoms, and *m* is a whole number greater than 6 the equivalent weight of the polymeric amine being no more than 14,000.

2. Cellulose ester fibers having wool dyeing properties essentially consisting of cellulose acetate and approximately 10–30%, of a polymeric amine which is a vicsose oil having the formula:



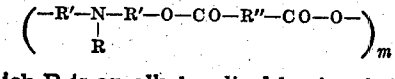
in which R is an alkyl radical having 1–4 carbon atoms, R′ is a saturated hydrocarbon radical having 2–4 carbon atoms, and of a structure such that at least 2 carbon atoms separate the N and O, R″ is a saturated hydrocarbon radical containing 1–8 carbon atoms, and *m* is a whole number greater than 6 the equivalent weight of the polymeric amine being no more than 14,000.

3. Cellulose ester fibers having wool dyeing properties essentially consisting of a lower fatty acid ester of cellulose and approximately 10–30%, of a viscous oil consisting of the polymer of a dicarboxylic acid and ethyl diethanolamine.

4. Cellulose ester fibers having wool dyeing properties essentially consisting of cellulose acetate and approximately 10–30%, of a viscous oil consisting of a polymer of a dicarboxylic acid and ethyl diethanolamine.

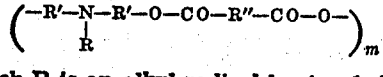
5. A spinning solution essentially consisting of

a lower fatty acid ester of cellulose and approximately 10–30%, of a polymeric amine which is a viscose oil having the formula:



in which R is an alkyl radical having 1–4 carbon atoms, R′ is a saturated hydrocarbon radical having 2–4 carbon atoms, and of a structure such that at least 2 carbon atoms separate the N and O, R″ is a saturated hydrocarbon radical containing 1–8 carbon atoms, *m* is a whole number greater than 6 the equivalent weight of the polymeric amine being no more than 14,000, and sufficient acetone to completely dissolve the cellulose ester and the polymeric amine.

6. A spinning solution essentially consisting of cellulose acetate and approximately 10–30%, of a polymeric amine which is a viscous oil having the formula:



in which R is an alkyl radical having 1–4 carbon atoms, R′ is a saturated hydrocarbon radical having 2–4 carbon atoms, and of a structure such that at least 2 carbon atoms separate the N and O, R″ is a saturated hydrocarbon radical containing 1–8 carbon atoms, *m* is a whole number greater than 6 the equivalent weight of the polymeric amine being no more than 14,000, and sufficient acetone to completely dissolve the cellulose ester and the polymeric amine.

7. A spinning solution essentially consisting of cellulose acetate, approximately 10–30%, of a viscous oil consisting of a polymer of dicarboxylic acid and ethyl diethanolamine and sufficient acetone to completely dissolve the cellulose acetate and the polymer.

JOHN R. CALDWELL.