

1

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COMPOSITION CONSISTING OF CELLULOSE ACETATE AND COPOLYMER OF N,N-DIMETHYL-ACRYLAMIDE

Harry W. Coover, Jr., Kingsport, Tenn., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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5 Claims. (Cl. 260-17)

This invention relates to the modification of cellulose acetate in order to improve certain of its properties and to impart thereto new properties.

Cellulose esters have little, if any, affinity for most wool dyes such as those dyes containing acid groups. This property is often disadvantageous since many of the wool dyes are easily applied and relatively cheap. Furthermore, the development of cellulose acetate staple fiber makes it particularly desirable to be able to dye such staple fibers with conventional wool dyes.

It has been realized that cellulose acetate is an excellent fiber for blending with wool; however, due to the fact that cellulose acetate has little if any affinity for wool dyes, acetate-wool blends can not be satisfactorily union dyed, and its use in such mixtures has been restricted. Dyeing of a material consisting of wool and cellulose acetate in the same dye bath has resulted very often in each of the components having a different color. Clearly, this is undesirable and the development of dyes suitable for these blends is both expensive and difficult. Furthermore, it has not been possible to successfully finish fabrics containing cellulose acetate with conventional textile finishing agents which are applied to other fabrics such as cotton and viscose in order to improve such properties as "hand," crease recovery and wrinkle resistance, and abrasion resistance. When formaldehyde-containing finishes, for example, are applied to cellulose acetate, they stay only on the surface of the acetate, giving a stiff, boardy fabric that has poor crease recovery and abrasion resistance.

Another characteristic of ordinary unmodified cellulose acetate in wool blends is that it does not lend itself to fulling. The "hand" of fabrics made from wool is enhanced by this process of fulling, which is related in part to the ability of wool to shrink under certain conditions. Ordinarily when other fibers such as unmodified cellulose acetate and the like are blended with wool, only the wool can be "fulled" and the resultant fabrics do not have a wool-like or luxuriant hand. Such fabric blends are said to have a "synthetic" or non-wool-like hand, a property which is generally not considered to be desirable.

In addition, many synthetic fibers have a cold or unnatural feel due to low "moisture regain" or the inability of the fibers when dried to take up moisture. Consequently, it is desirable to have a relative high "moisture regain" in order for fabrics to feel comfortable when in contact with the skin. Moreover, fibers which have a high "moisture regain" do not tend to build up static charges; accordingly, they process much more easily than fibers with a lower moisture regain, and are also less prone to soil, etc. in actual use.

I have made the discovery that cellulose acetate can be modified with homopolymers of N-alkylacrylamides and N-alkylmethacrylamides and copolymers polymerized from monomeric mixtures at least 65% by weight of

2

which are N-alkylacrylamides and N-alkylmethacrylamides to produce modified cellulose acetate fibers which make excellent blends with wool. These fibers have excellent affinity for direct, wool, acetate and vat dyes; therefore, they may be blended with wool, and the resultant blend of fibers dyed with the same dye. These union dyed fabrics or fibers exhibit washing and dyeing fastness properties equivalent to or better than those exhibited by dyed wool alone. The resultant fabric blend can also be "fulled" to improve its hand and to produce a more luxuriant material, which in some cases has a hand superior to that of wool alone.

Cellulose acetate modified according to my invention also has a higher moisture regain than regular cellulose acetate and therefore processes very easily in commercial equipment and has a more luxuriant hand than ordinary unmodified cellulose acetate. Fabrics made from cellulose acetate modified according to my invention also have a higher abrasion resistance than fabrics made from ordinary unmodified cellulose acetate. Another valuable property of cellulose acetate modified according to my invention is its ability to take up commercially available finishing agents to improve its hand and crease resistance and its abrasion resistance even further.

One object of this invention is to provide modified cellulose acetate having improved dyeing properties. Another object is to provide a modified cellulose acetate material which, when blended with wool, gives excellent union dyeings with wool dyes. An additional object is to provide a modified cellulose acetate material which, when blended with wool, can be fulled to give a fabric of luxuriant hand.

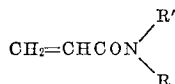
A further object is to provide a modified cellulose acetate material which has a higher moisture regain than ordinary unmodified cellulose acetate. Another object is to provide a modified cellulose acetate which exhibits improved processing characteristics and superior "hand," both alone and in blends with other materials such as wool. A further object is to provide a modified cellulose acetate material which has a higher abrasion resistance than ordinary unmodified cellulose acetate. Another object is to provide fabrics made from modified cellulose acetate alone and in blends with other materials such as wool which can be finished using resin finishes to further improve their "hand," wrinkle resistance and abrasion resistance.

The above objects of this invention are obtained by modifying cellulose acetate with homopolymers and copolymers of N-alkylacrylamides and N-alkylmethacrylamides and with copolymers polymerized from monomeric mixtures containing at least 65% of an N-alkylacrylamide or N-alkylmethacrylamide. The 65-100% must be either an N-alkylacrylamide, an N-alkylmethacrylamide, a mixture of different N-alkylacrylamides, a mixture of different N-alkylmethacrylamides, or a mixture of at least one N-alkylacrylamide and at least one N-alkylmethacrylamide. Copolymers as used herein includes polymeric compositions prepared from monomeric mixtures containing two or more monomeric materials.

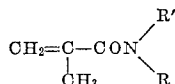
More particularly, the sole monomer or the monomer comprising the 65-100% of the monomeric mixture in the case of copolymers from which the polymers are prepared which are operative in my invention include water-soluble N-alkylacrylamides and N-alkylmethacrylamides with the exception of the N-butyl acrylamides and N-

3

butylmethacrylamides which are only slightly water-soluble. The homopolymer modifiers should include acrylamides having the structure



wherein R' is hydrogen or an alkyl group containing from 1-4 carbon atoms, and R is an alkyl group containing from 1-4 carbon atoms, and methacrylamides having the structure



wherein R' may be hydrogen or an alkyl group containing from 1-4 carbon atoms, and wherein when R' is hydrogen, R is an alkyl group containing 2-4 carbon atoms. When R' is an alkyl group containing from 1-4 carbon atoms, R is an alkyl group containing from 1-4 carbon atoms.

Copolymers of these acrylamides and methacrylamides which are valuable for use in this invention contain from 65-100% of the above-described amides. Suitable monomers for copolymerization with the amides are unsaturated compounds having the structure



In order for modifiers to be operable in my invention, they must not only be soluble in acetone, but must also be compatible with cellulose acetate. Compatibility of the polymers of this invention with cellulose acetate is completely unexpected since it is generally known that most polymers are not compatible with one another.

The compounds which may constitute up to 35% of the monomeric mixture from which the copolymer is prepared may be such compounds as vinyl esters, vinyl halides, acrylic and methacrylic acid derivatives such as nitriles, amides and esters, maleic and fumaric acid derivatives such as nitriles, amides, esters, mixed ester-amides and maleic anhydride. Preferably, the 0-35% of the monomeric mixture is made up of monomers which contain fewer than 20 carbon atoms.

The unsubstituted acrylamide, methacrylamide, and N-methylmethacrylamide homopolymers are insoluble in acetone and copolymers containing high concentrations thereof are not operable in my invention. However, when such amides are copolymerized with highly soluble acrylamides, copolymers containing relatively minor concentrations thereof are still soluble in acetone. In general, copolymers containing less than 15% of these particular amides are acetone-soluble and are compatible with cellulose acetate.

The homopolymer and copolymer modifiers of this invention can be prepared by homopolymerizing or copolymerizing the N-substituted acrylamides and methacrylamides by the usual methods, such as solution, emulsion and bulk polymerization using free-radical peroxide type or other suitable catalysts. The polymerizations can also be catalyzed by heat, ultraviolet light, etc. The modified cellulose esters can be prepared by either dissolving separately or together the amide modifier and the cellulose ester in acetone. If dissolved separately, the solutions are combined. The acetone solutions can then be spun into fibers either by a dry spinning or a wet spinning process.

Acetone-soluble cellulose acetate is cellulose acetate having an acetyl content of below about 42% and as used hereinafter in the examples and claims, cellulose acetate refers to both acetone-soluble cellulose acetate and cellulose acetate which is not completely soluble in acetone.

Cellulose acetate having an acetyl content of at least 42% is not completely soluble in acetone under normal conditions but is soluble in such solvents as methylene

4

chloride, dimethylformamide, dimethylacetamide, or a methylene chloride methanol mixture.

The modifiers described herein may also be used with cellulose acetate having an acetyl content above 42%, but these modifiers must also be soluble in solvents which dissolve this cellulose acetate. Accordingly, when this cellulose acetate is modified, it may be prepared by either dissolving separately or together the polyamide modifier and the cellulose acetate in methylene chloride, dimethylformamide, dimethylacetamide, or a methylene chloride/methanol mixture. If dissolved separately the solutions are combined. The cellulose acetate modified solutions can then be spun into fibers either by a dry spinning or a wet spinning process.

The following examples will further illustrate this invention:

Example 1

Fibers spun from an acetone solution of cellulose acetate containing 15% poly-N-isopropylacrylamide showed excellent affinity for acetate, direct, wool, and vat dyes. Acetate dyes which have poor gas fastness showed excellent gas fastness on these fibers.

Example 2

Fibers spun from an acetone solution of cellulose acetate containing 10% of poly-N,N'-dimethylacrylamide showed excellent affinity for acetate, direct, wool, and vat dyes. These fibers, which had a moisture regain of 8%, processed well on commercial spinning equipment and were made into a fabric which after dyeing had an excellent, wool-like hand.

Example 3

Fibers spun from an acetone solution of cellulose acetate containing 20% of poly-N-tert-butylacrylamide showed excellent affinity for direct, acetate, vat, and wool dyes.

Example 4

Fibers spun from an acetone solution of cellulose acetate containing 10% by weight of poly-N-methylacrylamide showed excellent affinity for direct, acetate, vat, and wool dyes. Blends of this fiber with wool gave excellent union dyeings with such wool dyes as Brilliant Milling Blue B (Prototype No. 37), Fast Red S, conc. (Color Index 176), and Milling Orange G (Color Index 377).

Example 5

Fibers spun from an acetone solution of cellulose acetate containing 20% by weight of poly-N,N-dimethylmethacrylamide showed excellent affinity for direct, acetate, vat, and wool dyes. Samples of the fibers or fabric dyed with Eastman Blue BNN (Prototype 228) exhibited excellent gas fastness. Unmodified cellulose acetate showed very poor gas fastness when dyed with this same dye.

Example 6

Fibers spun from an acetone solution of cellulose acetate containing 15% by weight of a copolymer of 80/20 N-ethylmethacrylamide/methyl acrylate showed excellent affinity for acetate, vat, and wool dyes.

Example 7

Fibers spun from an acetone solution of cellulose acetate containing 10% by weight of a copolymer of 90/10 N-isopropylacrylamide/acrylonitrile showed good affinity for acetate, vat, and wool dyes.

Example 8

Fibers spun from an acetone solution of cellulose acetate containing 15% of a copolymer of 85/15 N,N-dimethylmethacrylamide/vinyl acetate showed good affinity for direct, acetate, vat, and wool dyes. A 50/50 blend of this fiber with viscose gave an excellent union dyeing with Dark Orange G (Color Index 478).

5

Example 9

Fibers spun from an acetone solution of cellulose acetate containing 25% by weight of poly-N-methyl-N-ethylmethacrylamide showed excellent affinity for direct, acetate, vat, and wool dyes.

Example 10

Fibers spun from an acetone solution of cellulose acetate containing 15% by weight of a copolymer of 80/10/10 N,N-dimethylacrylamide/vinylidene chloride/methyl methacrylate showing excellent affinity for direct, acetate, vat, and wool dyes.

Example 11

Fibers spun from a methylene chloride solution of cellulose acetate having an acetyl content above 42% containing 15% of poly-N-isopropylacrylamide showed excellent affinity for acetate, direct, wool, and vat dyes.

Example 12

Fibers spun from a solution of cellulose acetate having an acetyl content above 42% and 20% of poly-N,N-dimethylacrylamide dissolved in a 90/10 methylene chloride/methanol mixture showed excellent affinity for acetate, direct, wool, and vat dyes and had excellent light fastness, especially in the case of the acid wool dyes.

Example 13

Fibers spun from a dimethylformamide solution of cellulose acetate having an acetyl content above 42% containing 15% of a copolymer of 75/25 N,N-dimethylacrylamide/N-isopropylacrylamide showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 14

Fibers spun from a methylene chloride solution of cellulose acetate having an acetyl content above 42% containing 10% of poly-N,N-dimethylacrylamide showed excellent affinity for direct, acetate, vat, and wool dyes.

Example 15

Fibers spun from an acetone solution of cellulose acetate containing 15% of a 75/25 N,N-dimethylacrylamide/N-isopropylacrylamide copolymer showed excellent affinity for acetate, direct, wool, and vat dyes and gave excellent union dyeings with wool. Wool dyes which ordinarily have poor light fastness showed excellent light fastness on these fibers. Fabrics made from these fibers took up commercial textile finishing agents to give materials having improved properties and an excellent "hand."

Example 16

Fibers spun from an acetone solution of cellulose acetate containing 10% of a 90/10 N,N-dimethylacrylamide/N-methylmethacrylamide copolymer showed excellent affinity for acetate, direct, wool, and vat dyes and gave excellent union dyeings with wool.

Example 17

Fibers spun from an acetone solution of cellulose acetate containing 20% of a 70/20/10 N,N-dimethylacrylamide/N-tertiary-butylacrylamide/N-isopropylacrylamide terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes and gave excellent union dyeings with wool.

Example 18

Fibers spun from an acetone solution of cellulose acetate containing 5 parts of a 99/1 N,N-dimethylacrylamide/acrylamide copolymer showed good affinity for acetate, vat, and wool dyes.

Example 19

Fibers spun from an acetone solution of cellulose acetate containing 30% by weight of an 85/15 N-isopropylacrylamide/N-methylmethacrylamide copolymer showed

6

excellent affinity for direct, acetate, wool, and vat dyes and gave excellent union dyeings with wool.

Example 20

Fibers spun from an acetone solution of cellulose acetate containing 20% of 70/20/10 N,N-dimethylacrylamide/N-isopropylacrylamide/maleic anhydride terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 21

Fibers spun from an acetone solution of cellulose acetate containing 20% of 70/20/10 N,N-dimethylacrylamide/N-isopropylacrylamide/diethyl fumarate terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 22

Fibers spun from an acetone solution of cellulose acetate containing 20% of 70/20/10 N,N-dimethylacrylamide/N-isopropylacrylamide/vinyl acetate terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 23

Fibers spun from an acetone solution of cellulose acetate containing 20% by weight of a 65/35 N,N-dimethylacrylamide/methylacrylate copolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 24

Fibers spun from an acetone solution of cellulose acetate containing 15% by weight of a 75/15/5/5 N,N-dimethylacrylamide/N-isopropylacrylamide/vinylidene chloride/vinyl acetate copolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 25

Fibers spun from an acetone solution of cellulose acetate containing 13% by weight of a 90/10 copolymer of N,N-dimethylacrylamide/methacrylamide copolymer showed good affinity for acetate, vat, and wool dyes.

Example 26

Fibers spun from an acetone solution of cellulose acetate containing 20% of a 75/15/10 N,N-dimethylacrylamide/N-isopropylacrylamide/fumaronitrile terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 27

Fibers spun from an acetone solution of cellulose acetate containing 20% of a 75/15/10 N,N-dimethylacrylamide/N-isopropylacrylamide/N,N,N',N'-tetramethylfumaramide terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Example 28

Fibers spun from an acetone solution of cellulose acetate containing 20% of a 75/15/10 N,N-dimethylacrylamide/N-isopropylacrylamide/N-methylmaleamate terpolymer showed excellent affinity for direct, acetate, wool, and vat dyes.

Cellulose acetate compositions containing from 5-30% by weight of the homo- or copolymer modifiers of this invention can be used. However, the preferred range is 10-30 parts by weight. Cellulose acetate modified according to the process of this invention when spun into fibers show good to excellent affinity, depending on the concentration of modifier, for all classes of dyes and are particularly outstanding in that wool dyes have excellent light fastness.

The particular dyes referred to in the examples are merely incidental to a showing of the particular adaptability of our invention, but other commonly available dyes for wool or acetate may be substituted to illustrate the unusual dyeing qualities of these fibers.

Wherever a percentage is indicated herein in the speci-

7

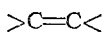
fication and claims, it is intended and should be understood to be by weight.

Cloth manufactured from fibers modified according to this invention possesses the excellent properties found in the fabrics made from cellulose ester fabric. Blended with natural fiber such as wool, the resulting fabric combines the advantages of both materials, for instance, combining the high elasticity of the natural fiber with the high ductility of the cellulose fiber such as cellulose acetate or cellulose triacetate. As a result of this invention, the possible combinations are great in number and have widespread utility, particularly in the apparel field.

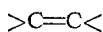
This application is a continuation-in-part of United States application Serial No. 368,807, filed July 17, 1953.

I claim:

1. A composition of matter consisting of 70-95% cellulose acetate and 5-30% of an acetone-soluble copolymer prepared from a monomeric mixture containing at least 65% N,N-dimethylacrylamide with at least one unsaturated compound having the structure:



in which the compounds having the grouping:



are selected from the class consisting of vinyl esters, vinylidene chloride, maleic and fumaric esters, maleic and fumaric amides, and maleic and fumaric nitriles, mixed ester-amides of fumaric and maleic acids, and maleic anhydride, acrylic and methacrylic amides and nitriles, which

8

class is made up of monomers which contain fewer than twenty carbon atoms.

2. A composition of matter consisting of 70-95% cellulose acetate and 5-30% of an acetone-soluble copolymer prepared from a monomeric mixture containing substantially 75% N,N-dimethylacrylamide and 25% N-isopropylacrylamide.

3. A composition of matter consisting of 70-95% cellulose acetate and 5-30% of an acetone-soluble copolymer prepared from a monomeric mixture containing substantially 65% N,N-dimethylacrylamide and 35% methylacrylate.

4. A composition of matter consisting of 70-95% cellulose acetate and 5-30% of an acetone-soluble copolymer prepared from a monomeric mixture containing substantially 70% N,N-dimethylacrylamide, 20% N-isopropylacrylamide and 10% vinyl acetate.

5. A composition of matter consisting of 70-95% cellulose acetate and 5-30% of an acetone-soluble copolymer prepared from a monomeric mixture containing substantially 80% N,N-dimethylacrylamide, 10% vinylidene chloride and 10% methylmethacrylate.

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