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MODIFIED SPINNING SOLUTIONS, METHODS FOR PRODUCING FIBERS AND FILMS, AND FILMY PRODUCTS PRODUCED THEREFROM

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The present invention is concerned with the modification of cellulosic spinning solutions and is particularly concerned with the modification of viscose and cuprammonium cellulose solutions and a process for producing improved cellulose fibers and films from such solutions. The present application is a continuation-in-part of my copending U.S. application Serial No. 157,267, filed December 5, 1961, now abandoned.

One of the objects of the present invention is to provide a process for producing regenerated cellulose fibers, filaments, and yarns which are characterized with improved crease-resistance as compared to conventional cellulose fibers and the like obtained from corresponding spinning solutions. Another object of the invention is to provide a process for producing regenerated cellulose articles of decreased water-sensitivity and decreased cross-sectional swelling on immersion in water. Another object of the invention is to provide a process for producing regenerated cellulose articles having reduced water-retentivity and having improved resistance to progressive dimensional shrinkage on repeated laundering. Other objects of the invention will appear hereinabove.

It has heretofore been proposed in U.S. Patent 2,173,005 to impregnate a gel rayon with N-methylolmethacrylamide. The impregnation was effected in the presence of an acid and the impregnated product was dried and then heated at an elevated temperature. It has also been proposed in U.S. Patent 2,858,185 to incorporate into a viscose or cuprammonium spinning solution a polymer of acrylamide or a methylolated acrylamide polymer. After spinning the resulting solutions reaction was effected in the presence of an acid by heating the formed composition and applying formaldehyde when the polymer used in the spinning solution was not methylolated. The latter patent points out that when a low molecular weight resin precondensate is incorporated in viscose, about 80 to 90 percent of the precondensate is lost because it is leached out in the acid spinning bath.

In accordance with the present invention, it has been found that N-methylolacrylamide, N-methylolmethacrylamide, a lower (C_1–C_4) alkyl ether of one of these amides, or a mixture of any two or more of these compounds can be incorporated into a cellulosic spinning solution provided it is strongly alkaline and that such a solution can then be spun into an aqueous salt or acid bath to coagulate and/or regenerate cellulosic components without encountering such excessive losses of the monomer as occurred when resin precondensates were heretofore used. This is surprising because of the fact that the monomers are well known to be subject to hydrolysis in strongly alkaline media.

In accordance with the present invention these results are accomplished by introducing into a spinning solution of alkaline character such as viscose or cuprammonium cellulose a small amount of N-methylolacrylamide, N-methylolacrylamide, a lower (C_1–C_4) alkyl ether of one of these amides, or a mixture of any two or more of these compounds. The proportion of this amide additive may be from 1 to 25% by weight based on the weight of cellulose in the spinning solution. Preferably the amount is from 5 to 10% by weight on the cellulose. The amide is introduced into the spinning solution soon before it is to be spun so as to avoid excessive hydrolysis of the amide linkage which would convert the compound into an acid. Under the alkaline conditions of the cellulose spinning solutions, the N-substituted acrylamide apparently forms a derivative of cellulose containing a plurality of amide-containing units according to the following equation:

$$\mathrm{R(OH)_x + H_2C{=}C(R^\circ)CONHCH_2OR'} \rightarrow \mathrm{R(OCH_2{-}CH(R^\circ)CONHCH_2OR')_x}$$

wherein R is a cellulosic residue, e.g. of cellulose xanthate or of cuprammonium cellulose.

R° is selected from the group consisting of hydrogen and methyl, R' is selected from the group consisting of hydrogen and alkyl groups having 1 to 4 carbon atoms, and

x is the degree of substitution which may be from 0.15 to 0.60 per glucose unit in R.

The modified cellulose in a cuprammonium cellulose solution is an N-methylol-β-amidoethyl ether or an N-methylol-β-methyl-β-amidoethyl ether of cuprammonium cellulose depending on whether N-methylolacrylamide or N-methylolmethacrylamide is combined with the cuprammonium cellulose. In the case of the modified viscose, the compound in the spinning solution is an N-methylol-β-amidoethyl ether or an N-methylol-β-methyl-β-amidoethyl ether of cellulose xanthate. When an N-alkoxymethyl-acrylamide or -methacrylamide is used instead of the N-methylol derivatives, the modified cellulose contains N-alkoxymethyl-β-amidoethyl or N-alkoxymethyl-β-methyl-β-amidoethyl groups connected to the cellulose residue through an ether atom. Preferred alkoxymethyl groups are methoxymethyl, ethoxymethyl, isopropoxymethyl, and tert-butoxymethyl. As previously stated, the degree of substitution with the ether groups named may be from 0.15 to 0.60 per glucose unit in the cellulose derivative.

In the systems of U.S. Patent 2,858,185 a polymeric material of considerably different constitution is used for cross-linking the cellulose. Because of the great difference in chemical constitution between the cross-linking polymer and the cellulose to be cross-linked, stretching of the mixture of these polymers cannot orient the molecules of cellulose and cross-linking polymers as effectively as stretching of a single type of material such as cellulose itself. Furthermore the difference in the character of the cellulose and polymeric material tends to produce an uneven distribution of cross-linkages in the final product.

In accordance with the present invention the cross-linking material as well as the material being cross-linked are essentially slightly modified cellulose derivative compounds. With such a material the stretching is able to introduce a larger proportion of crystalline zones to the stretched products and the cross-linking bonds are more uniformly distributed. The present invention accordingly is able to provide improved products in respect to tensile strengths and in respect to homgeneity.

The methylolated or alkoxymethyl-substituted unsaturated amide may be mixed into the spinning solution after it has been aged just shortly before it is fed to the spinnerets or film-forming extrusion devices. Advantageously the amide may be introduced by injecting an aqueous solution thereof into the spinning solution as it flows through the feed line to the spinneret or other forming device such as at a point in the pump supply line at a distance of six inches to several feet before the spinneret.

The composition of the spinning solution may be any of those normally used in the viscose or cuprammonium cellulose spinning art. For example, when viscose is used it may have any spinnable composition and may be a normal viscose having a sodium chloride salt test value of from 3 to 6, containing from 6 to 9 sodium hydroxide and of normal spinning viscosity, e.g., having a ball fall viscosity of 35 seconds at 18° C.

The setting bath into which the modified viscose is extruded may be a coagulating and cellulose-regenerating bath of the composition normally used in the manufacture of fibers or yarns from viscose. Aqueous baths containing from 7 to 13.5% sulfuric acid and from 18 to 28% sodium sulfate are satisfactory. The bath may also contain comparatively small amounts, for example, from 0.1 to 5% of zinc sulfate, as well as small amounts of other adjuvants or assistants.

In the case of a cuprammonium cellulose solution any of the normal coagulating baths used in that type of process may be employed.

Regardless of what spinning operation is used, the films, filaments or yarn produced may be stretched longitudinally or, in the case of a film, longitudinally and laterally. The amount of stretch may vary widely depending on the particular conditions to which the formed articles are subjected during the stretching. Stretching is preferably effected on the filaments or films while they are submerged in or sprayed with hot water or other heated aqueous baths which may contain acids or salts and under these conditions stretch may amount to as much as 70 to 100% of the original length of the filaments. Stretching may be effected at any point but is usually effected right after the yarn leaves the coagulating bath and/or regenerating bath. After being stretched the yarn may be subjected to the usual purification steps associated with the particular process. For example, in the case of the viscose process the stretched yarn may be washed, desulfurized, and bleached, and then may finally have a lubricant or softening composition applied before drying.

In accordance with the present invention the stretched and purified yarn is treated with an acid catalyst for effecting reaction of methylol or alkoxymethyl groups with hydroxyl groups of the cellulose to effect cross-linking thereof. The alkoxymethyl groups generate methylol groups under the conditions required for the reaction of the methylol groups and the hydroxyl groups of the cellulose. Examples of preferred catalysts are ammonium chloride, monobasic and dibasic ammonium phosphates and oxalic, lactic, citric, tartaric, formic, acetic, propionic, boric, and succinic acids. Salts of amines, such as 2-amino-2-methyl-propanol-1, with acids, such as hydrochloric or sulfuric acid, may be used. The catalyst may be applied as an aqueous solution of a concentration from about ¼ to 3% by weight. The film or filaments of the modified cellulose may be passed through a bath of the catalyst solution or the catalyst solution may be sprayed onto the film or filament after it passes from the usual liquid after-treating stages but prior to the drying stage.

After application of the acid catalyst the treated filament or film is dried and then heated to a temperature of 220° to 350° F. for a period of at least 30 seconds and up to five minutes. At this temperature the hydroxyl groups of the modified cellulose react with the methylol groups thereof (or the methylol groups generated from the alkoxymethyl groups therein) to form linkages, thereby cross-linking the cellulose molecules in the product.

The effect on the object depends upon the proportion of unsaturated amide introduced into the spinning solution. The use of as little as 1% serves to reduce the water-rentention and the tendency of the filament or film to swell and shrink on exposure to water. When 5 to 10% by weight of unsaturated amide is used it has been found that the products show greatly improved resistance to shrinkage and creasing or wrinkling.

The following examples, in which parts and percentages are by weight unless otherwise stated, are illustrative of the present invention.

Example 1

A viscose spinning solution containing 6% by weight of cellulose and 7% sodium hydroxide is aged 96 hours and then 5% by weight, based on the weight of the cellulose, of N-methylolacrylamide is added to the viscose. Within 30 minutes after the addition the modified viscose is spun into a coagulating and regenerating bath containing 10% sulfuric acid and 20% sodium sulfate at 50° C. The spun yarn is stretched between two godets rotating at different speeds such that the second and faster godet operates at 60% higher speed than the first godet, hot water at a temperature of 80° C. being poured over the yarn on the first godet. The yarn is then passed through the usual liquid after-treating process and finally treated with a solution containing 10% by weight of ammonium chloride and dried. After drying at 300° F. for five minutes the final yarn is insoluble in cuprammonium hydroxide solutions. The yarn shows improved crease-resistance and resistance to shrinking on exposure to water as compared to a yarn made in the same way but without the amide additive.

Example 2

The procedure of Example 1 is repeated using

(*a*) 15% by weight, based on cellulose, of N-methylolmethacrylamide;

(*b*) 10% by weight, based on cellulose, of N-methoxymethylacrylamide;

(*c*) 13% by weight, based on cellulose of N-tert-butoxymethylacrylamide.

Similar results are obtained.

Example 3

To a cuprammonium cellulose solution containing 3.8% cellulose and 30 grams of ammonia per liter, there is added 7% (based on cellulose) of N-methylolacrylamide. The solution obtained is spun within 30 minutes into an aqueous 4% sodium hydroxide precipitating bath. The yarn is neutralized, rinsed, stretched between godets while being subjected to hot water at 70° C. as in Example 1, and then sprayed with an aqueous 1% solution of oxalic acid. It is then dried and heated to 300° F. for five minutes. The product shows good crease-resistance and resistance to shrinkage on washing.

Example 4

A viscose spinning solution containing 6% by weight of cellulose and 7% sodium hydroxide is aged 96 hours and then 25% by weight, based on the weight of the cellulose, of N-methylolacrylamide is added to the viscose. Within 30 minutes after the addition, the modified viscose is spun into a coagulating and regenerating bath containing 10% sulfuric acid and 20% sodium sulfate at 50° C. The spun yarn is stretched between godets rotating at different speeds so that the second and faster godet operates at 60% higher speed than the first godet, hot water at a temperature of 80° C. being poured over the yarn on the first godet. The yarn is then passed through the usual liquid after-processing baths and finally treated with a solution containing 10% by weight of ammonium chloride and dried. After drying at 300° F. for five minutes the final yarn is insoluble in cuprammonium hydroxide solutions. The yarns had improved crease-resistance and resistance to shrinking on exposure to water as compared to a yarn made in the same way but without the amide additive.

Example 5

Example 4 was repeated except that 50% of N-methylolacrylamide was used instead of 25%.

Example 6

Example 4 was repeated except that 50% N-methylolacrylamide was used instead of 25% and modified viscose was spun 10 minutes after the addition of the N-methylolacrylamide.

I claim:

1. A method of producing a cross-linked regenerated cellulose filmy product which comprises adding at least one compound selected from the group consisting of N-methylolacrylamide, N-methylolmethacrylamide and the (C_1–C_4)-alkyl ethers thereof to an alkaline solution selected from the group consisting of viscose and cuprammonium cellulose solutions to form therein a modified cellulosic compound having the formula

$$R(OCH_2—CHR^\circ CONHCH_2OR')_x$$

wherein

R represents a residue of a compound selected from the group consisting of cellulose xanthate and cuprammonium cellulose,
R° is selected from the group consisting of H and methyl,
R′ is selected from the group consisting of hydrogen and alkyl groups having 1 to 4 carbon atoms, and
x is 0.15 to 0.60 per glucose unit of R,

extruding the solution containing the modified cellulosic compound into a coagulating bath to form a filmy product, regenerating the residue R to a modified cellulosic compound of the formula above wherein R is a regenerated cellulose residue, stretching the regenerated product at least in a longitudinal direction, subsequently treating the filmy product with an acidic catalyst, and then drying and heating the filmy product at a temperature of at least 220° F. for a period of at least ½ minute.

2. As an article of manufacture, a cross-linked cellulosic product obtained by the process of claim 1.

3. A method of producing a cross-linked regenerated cellulose filmy product which comprises adding N-methylolacrylamide to an alkaline viscose solution to form therein a modified cellulosic compound having the formula

$$R(OCH_2—CH_2CONHCH_2OH)_x$$

wherein

R represents a residue of cellulose xanthate and x is 0.15 to 0.60 per glucose unit of R,

extruding the solution containing the modified cellulosic compound into a coagulating bath to form a filmy product, regenerating the residue R to a modified cellulosic compound of the formula above wherein R is a regenerated cellulose residue, stretching the regenerated product at least in a longitudinal direction, subsequently treating the filmy product with an acidic catalyst, and then drying and heating the filmy product at a temperature of at least 220° F. for a period of at least ½ minute.

4. A method of producing a cross-linked regenerated cellulose filmy product which comprises adding N-methylolacrylamide to a cuprammonium cellulose solution to form therein a modified cellulosic compound having the formula

$$R(OCH_2—CH_2CONHCH_2OH)_x$$

wherein

R represents a residue of cuprammonium cellulose and x is 0.15 to 0.60 per glucose unit of R,

extruding the solution containing the modified cellulosic compound into a coagulating bath to form a filmy product, regenerating the residue R to a modified cellulosic compound of the formula above wherein R is a regenerated cellulose residue, stretching the regenerated product at least in a longitudinal direction, subsequently treating the filmy product with an acidic catalyst, and then drying and heating the filmy product at a temperature of at least 220° F. for a period of at least ½ minute.

5. A method for producing a cross-linked filmy product consisting essentially of a substituted regenerated cellulose having a degree of substitution from 0.15 to 0.6 per glucose unit which comprises the step of extruding through an orifice into a precipitating bath a solution of at least one cellulosic compound selected from the group consisting of those having the formula

$$R(OCH_2—CHR^\circ CONHCH_2OR')_x$$

wherein

R represents a residue of a compound selected from the group consisting of cellulose xanthate and cuprammonium cellulose,
R° is selected from the group consisting of H and methyl,
R′ is selected from the group consisting of hydrogen and alkyl groups having 1 to 4 carbon atoms, and
x is 0.15 to 0.60 per glucose unit of R,

to form a filmy product, stretching the filmy product, subsequently treating the stretched product with an acid catalyst, and then drying and heating the catalyst-treated product at a temperature of 220° to 350° F. for a period of about 30 seconds to 5 minutes to effect reaction of methylol groups with hydroxyl groups and resultant cross-linking of the cellulosic product.

6. As an article of manufacture, a cross-linked cellulosic product obtained by the process of claim 5.

7. A method for producing a cross-linked filmy product consisting essentially of a substituted regenerated cellulose having a degree of substitution from 0.15 to 0.6 per glucose unit which comprises the step of extruding through an orifice into a precipitating bath a solution of N-methylol-β-amidoethyl ether of cellulose xanthate, in which the degree of substitution by the ether attached groups is from 0.15 to 0.6 per glucose unit, stretching the filmy product, subsequently treating the stretched product with an acid catalyst, and then drying and heating the catalyst-treated product at a temperature of 220° to 350° F. for a period of about 30 seconds to 5 minutes to effect reaction of methylol groups with hydroxyl groups and resultant cross-linking of the cellulosic product.

8. A method for producing a cross-linked filmy product consisting essentially of a substituted regenerated cellulose having a degree of substitution from 0.15 to 0.6 per glucose unit which comprises the step of extruding through an orifice into a precipitating bath a solution of N-methylol-β-amidoethyl ether of cuprammonium cellulose, in which the degree of substitution by the ether attached groups is from 0.15 to 0.6 per glucose unit, stretching the filmy product, subsequently treating the stretched product with an acid catalyst, and then drying and heating the catalyst-treated product at a temperature of 220° to 350° F. for a period of about 30 seconds to 5 minutes to effect reaction of methylol groups with hydroxyl groups and resultant cross-linking of the cellulosic product.

9. A method of producing a cross-linked regenerated cellulose filmy product which comprises adding at least one compound selected from the group consisting of N-methylolacrylamide, N-methylolmethacrylamide and the (C_1–C_4)-alkyl ethers thereof to an alkaline solution selected from the group consisting of viscose and cuprammonium cellulose solutions to form therein a modified cellulosic compound, extruding the solution containing the modified cellulosic compound into a coagulating bath to form a filmy product, regenerating the modified cellulosic compound to a modified regenerated cellulose, stretching the regenerated product at least in a longitudinal direction, subsequently treating the filmy product with an acidic catalyst, and then drying and heating the filmy product at a temperature of at least 220° F. for a period of at least ½ minute.

10. As an article of manufacture, a cross-linked cellulosic product obtained by the process of claim 9.

References Cited in the file of this patent

UNITED STATES PATENTS

2,363,019 Schurmann et al. ______ Nov. 21, 1944