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2,686,103

PROCESS OF MODIFYING REGENERATED
CELLULOSE AND PRODUCT RESULTING
THEREFROM

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This invention relates to methods and means for modifying cellulosic materials and to the novel cellulosic compositions resulting therefrom. More particularly, it relates to the manufacture of viscose rayon modified with a polymeric acid compound, such as an interpolymer of styrene/maleic anhydride or derivative thereof. The invention is applicable to any type of regenerated cellulose rayon, but for the sake of convenience will be described in its specific applications to yarn produced by the viscose process.

In the textile industry it is well known that regenerated cellulose yarn lacks resilience, water repellency and affinity for acid dyestuffs. Frequently, it is desirable to mix rayon yarns with natural wool yarns in the production of fabrics, but this practice has been limited because of the inability of rayon yarns to be dyed with acid-wool dyes, the result being undesirable differences in coloration of the fabric. Still further, although rayons, in general, can be dyed with the same type of dyestuffs as those used on cotton, difficulties occur in the dyeing of rayon/cotton mixtures because of the greater affinity for the dyestuff and the lower wet strength of the rayon.

It has been thought to overcome these inherent drawbacks in viscose rayon yarn by the addition of substances to the viscose spinning solution capable of imparting to the rayon a more wool-like character and, at the same time, increase its affinity for acid dyestuffs and water repellency. However, while the rayon yarns produced in such manner have exhibited one or so of the desirable properties, they have been defective from the standpoint of tensile strength, color fastness and lack of quality uniformity. The loss of substantial amounts of the adjuvant material during spinning and washing operations plus the difficulties encountered in final purification of the resultant yarns have been stumbling blocks to the advances in this field.

It has been a desideratum to incorporate in the cellulose yarn structure reactive groups which may be used for chemically modifying the yarn without deleteriously effecting its tenacity, elongation, flex life and work recovery and yet impart to the yarn the desirable characteristics that it normally lacks, such as, for example, resilience, superior hand, receptivity to acid dyestuffs, water repellency, and insolubility. A con-

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siderable portion of the prior art in this field appears to have been directed towards enhancing the dyeability of viscose yarn. For example, in U. S. Patent 2,371,032, an attempt has been made to provide a procedure for obtaining dyeings on rayons of unusual fastness and levelness without recourse to severe processing conditions and a minimum of handling on the part of the dyer. The patent teaches that the maleic anhydride-styrene copolymer should first be condensed with an aromatic amine, capable of reacting with a diazonium compound, and then added to standard commercial viscose to the extent of only 5% (based on weight of cellulose) or less. This procedure is restricted to additions of small quantities of the condensation product due to its diminishing solubility (and eventual incompatibility) in the viscose solution as the percentage of material added is increased. Although many suggestions have also been made heretofore for rendering rayon textile materials water repellent by employing a variety of substances as textile treating agents, in general, such treatments have proved defective inasmuch as the yarn has not been permanently treated to withstand laundering, dry cleaning, etc.

The invention has as an object the provision, as new articles of manufacture, of funicular structures comprising regenerated cellulose and a substantial amount of styrene-maleic anhydride interpolymer or derivative thereof as well as the method of making the same. Another object of the invention is to incorporate with viscose a polymerization product obtainable from polymerizable olefinic compounds and ethylene-alpha-beta-dicarboxylic acids or anhydrides and after-treating the yarns with aliphatic and aromatic amines. A further object of the invention is to produce viscose yarn having improved hand, affinity for wool dyestuffs, water repellency, resilience and insolubility in usual cellulose solvents. A still further object is to prevent the loss of the styrene-maleic anhydride interpolymer from the yarn during washing by performing the operation under tension. Further objects of the invention are the manufacture of improved rayon yarns by coagulating and regenerating a viscose solution containing the sodium salt of a styrene-maleic anhydride interpolymer and then heating the modified cellulose-S/MA

yarn to produce a cross-linked insoluble product. Other objects of this invention will be apparent to those skilled in the art from a study of the specification.

The foregoing objects of this invention are obtained by mixing viscose with up to about 50% (by weight of the total yarn solids) of a salt of a polymeric acid or anhydride derived from alpha, beta dicarboxylic acid derivatives, such as styrene/maleic anhydride interpolymers (S/MA), spinning the regenerated composition in the usual manner, and then optionally washing the yarn under tension or prior to washing subjecting it to one of the following setting after-treatments: (1) insolubilizing by heating in an inert medium, (2) reacting with aliphatic or aromatic amines, either mono- or di-functional or similar reactive compounds, such as the alcohols like butyl or octyl alcohol, and (3) soaking and subsequently heating the yarn in an ammonium salt solution.

According to the preferred practice of the invention, there is employed the sodium salt of the S/MA interpolymers prepared by such processes as those shown in Graves U. S. 2,205,882 and Voss and Dickhauser U. S. 2,045,398.

In order to describe the invention more fully the following examples, which are not to be construed as limiting the scope, of the invention are given.

Example I

A solution was prepared using 12.8 parts of styrene-maleic anhydride copolymer having a polymerization index of 150 seconds, 0.43 part of 50% caustic and 160 parts of distilled water containing 0.17 part of a wetting agent, Duponol ME. This solution was mixed with 2570 parts of viscose of 5% cellulose-9% caustic composition. The viscose/polymeric anhydride solution was spun from a spinneret of 40 holes (0.0030 hole diameter) using an extrusion rate of 4.1 g. per minute into a bath at 60° C. composed of 20% sodium dihydrogen phosphate and 10% sodium sulfate adjusted with phosphoric acid to a pH of 3.0. After passing around a snubbing bar located under the bath, the yarn was collected on a bobbin at 550 inches per minute, regenerated in a phosphate bath like the spinning bath but at 100° C., and then washed in water. The yarn, which was not subjected to any after-treatment, was analyzed by extraction and titration and found to contain only about 2.5% of the constituent derived from the styrene-maleic anhydride, the balance having dissolved out during spinning and washing. The physical properties of the yarn were essentially normal. This illustrates that mere impregnation is insufficient. The following experiment shows a setting treatment:

The sodium salt of S/MA was added to viscose in an amount equal to 50% by weight of the total yarn solids and spun in a bath containing 9% sulfuric acid and 22% sodium sulfate and heated to 50° C. The yarn was then drawn 83% and thereafter regenerated in a 20% zinc sulfate bath maintained at 50° C. After having collected the yarn on a bobbin at the rate of 822 inches per minute, it was rinsed in a saturated solution of ammonium sulfate (brought to a pH of 8 with ammonium hydroxide) until acid-free. After being air-dried, the S/MA-cellulose yarn was refluxed for a period of three hours in a xylene solution of hexamethylene diamine. The final yarn had a pronounced affinity for wool dyestuffs, whereas similarly prepared yarns

not containing the S/MA constituent had practically no such affinity. The yarn was insoluble in cuprammonium solution. The yarn also had improved resilience and improved recovery from bending deformation and possessed the following physical properties: Denier 297, dry tenacity 1.51 g. p. d., wet tenacity 0.74 g. p. d., and loop tenacity 1.40 g. p. d. The elongation was 11.9% dry, 15.0% wet and 11.2% loop. The work recovery at a 0.76% stretch was 0.48. These physical properties are substantially as good as those customarily obtained on yarns using viscose only in standard textile viscose production.

Example II

A portion of the viscose/polymeric acid yarn of Example I was heated in xylene without the diamine whereby ester cross-linkages and anhydride groups were produced. This made the yarn insoluble in customary solvents such as cuprammonium solution, dimethyl dibenzyl ammonium hydroxide solution or 2.4 normal triethyl sulfonium hydroxide solution.

Example III

Another portion of the unreacted S/MA salt-cellulose yarn of Example I was soaked in a solution of ammonium sulfate prior to washing, and heated while immersed in the salt solution. This presumably resulted in the formation of imide groups of S/MA, i. e., styrene-maleimide, an inert and relatively water insensitive substance. The cellulosic yarn containing the reacted S/MA was then washed with water to remove the salts and residual spinning salt without loss of the S/MA constituent.

The imide formation by way of the ammonium salt as illustrated in above example may also be performed on the dry yarn for modifying its properties. If the initial spinning had taken place in a bath high in ammonium salt content, then the ammonium salt of the S/MA constituent would be formed at the time of the spinning and no specific soaking in ammonium salt solution would be required.

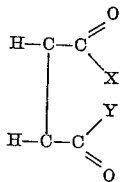
The preferred technique of washing the S/MA modified rayon yarn is to carry on the operation while the yarn is maintained under tension. This procedure prevents excessive loss of soluble S/MA salt.

The incorporation of chemically bound, water-repellent groups into a regenerated cellulose yarn containing S/MA may be carried out by allowing the modified yarn to react with aliphatic monoamines, such as stearyl amine, for example in the manner of Example I but substituting the monoamine for the hexamethylene diamine there used. Other aliphatic amines, preferably lower in molecular weight such as methyl amine, butyl amine, dimethyl amine or benzyl amine, may be employed to render the S/MA constituent of the modified rayon yarn water-insoluble prior to washing and to modify yarn properties, for example to produce softer yarn of reduced modulus more or less in proportion to the chain length of the aliphatic amine employed. It is believed that this insolubility is due to at least partial imide formation.

Cross-linking of S/MA modified viscose yarn with diamines, such as hexamethylene diamine, results in a more resilient polyamide type of product. If an excessive amount of diamine is originally employed in this reaction, free amine groups may remain in the yarn with the result

that the acid dyeing characteristics of the yarn are substantially enhanced.

Instead of using a polycarboxylic acid prepared by the reaction of maleic anhydride and styrene, there may be used any of the polycarboxylic acids prepared by the reaction of a compound of the following formula:



wherein X stands for OH, O-alkyl, O-aryl, or halogen and Y for OH or X and Y together stand for oxygen. When added to the alkaline viscose these derivatives are converted in part or totally into soluble sodium salts. Instead of the styrene, similarly, there may be used any organic compound capable of being polymerized and containing a single



grouping. The preparation of these compounds is specifically described in Voss and Dickhauser U. S. 2,047,398. As typical of the materials which may be used instead of maleic anhydride, there may be used, for instance, ethylene-alpha-beta-dicarboxylic acids such as maleic acid, fumaric acid, itaconic acid, citraconic acid, phenyl-maleic acid, benzyl-maleic acid, dibenzyl-maleic acid, etc. As examples of materials which may be used instead of styrene, there may be listed vinyl esters, vinyl ethers, vinyl halides, acrylic acids and its esters and the like.

The conditions used in the various steps in this invention may, of course, also be varied considerably. For example, the invention may be applied in the production of yarns, films, staple or flock useful in the production of felted or non-woven articles. The modified viscose may be regenerated directly or merely coagulated first and then regenerated. Further, the setting treatment may vary from a few minutes to several hours depending on the temperature which can be from about 80° to about 150° C. The modified article can contain from about 5% to about 50% of the modifier, based on the weight of the final product. In producing an article containing 50% of the modifier, about 60% of the modifier is incorporated initially due to loss during washing. If no setting treatment is used, such as heating or reacting with amines, ammonium salts or alcohols, it is preferred to wash under tension to diminish loss of modifier.

The dyed yarn produced as a result of treating the mixed S/MA viscose yarn with organic amines may be put to any use that ordinary textile rayons are used for. The ability of the modified regenerated cellulose yarn to accept acid wool dyes permits the mixing of yarns of this invention with natural wool yarns in the manufacture and coloration of fabrics. As the result of the processes and after-treatments hereinabove described, cellulosic yarns may be beneficially modified within wide limits by suitable choice of reactants to give yarns having improved hand, resilience, water repellency, flex life and water insolubility. In view of its improved properties, S/MA modified rayon yarn has wide potential use.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. A process for modifying regenerated cellulose which comprises adding to viscose from about 5% to about 50% by weight based on total solids of a water-soluble salt of a polymeric acid compound derived from an ethylene alpha, beta dicarboxylic acid; spinning the resultant blend into a coagulant to form a cellulose/polymeric acid composition; and then converting said polymeric acid constituent to an insoluble derivative from the group consisting of an ester, an imide and an amide.

2. A process in accordance with claim 1 wherein said composition is washed under tension prior to said converting.

3. A process in accordance with claim 1 wherein the converting is accomplished by heating the said regenerated cellulose/polymeric acid composition to form ester groups.

4. A process in accordance with claim 1 wherein the converting treatment is accomplished by forming the ammonium salt of the said regenerated cellulose/polymeric acid composition and heating the ammonium salt to form imide groups.

5. A process in accordance with claim 1 wherein the said converting is accomplished by heating the said regenerated cellulose/polymeric acid composition with an amine.

6. A process for modifying regenerated cellulose which comprises adding to viscose from about 5% to about 50% by weight based on total solids of the sodium salt of styrene-maleic anhydride copolymer; extruding the resultant mixture into a coagulating bath; regenerating the resultant coagulated cellulose which contains said copolymer; and then converting said copolymer to an insoluble form.

7. A process in accordance with claim 6 wherein the temperature used in the said converting is from about 80° C. to about 150° C.

8. A modified cellulose funicular body produced by extrusion of a viscose which contains from about 5% to 50% by weight on total solids of a water-soluble salt of a polymeric acid compound derived from an ethylene, alpha, beta dicarboxylic acid into a coagulating bath, followed by regeneration of the coagulated modified cellulose and conversion of the polymeric ethylene, alpha, beta dicarboxylic compound to an insoluble form.

9. The modified cellulose funicular body of claim 8, wherein the water-soluble salt of the polymeric acid compound is the sodium salt of a styrene-maleic anhydride copolymer.

10. The modified cellulose funicular body of claim 9, wherein the insoluble form is an ester.

11. The modified cellulose funicular body of claim 9, wherein the insoluble form is an imide.

12. The modified cellulose funicular body of claim 9, wherein the insoluble form is an amide.

References Cited in the file of this patent

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