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TEXTILE MATERIAL OF REGENERATED CELLULOSE CONTAINING A POLYACRYLAMIDE

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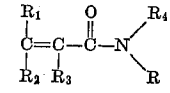
This invention relates to an improved textile material of regenerated cellulose, such as fibers, filaments, yarns, fabrics and the like, which contain certain polymers of acrylamide. This application is a continuation-in-part of my copending application Serial No. 266,243, filed January 12, 1952, now U.S. Patent No. 2,858,185, granted October 28, 1958, which discloses the production of regenerated cellulose fibers containing such polymers of acrylamide and claims the treatment with formaldehyde of the regenerated cellulose fibers and fabrics made therefrom which contain such polymers of acrylamide.

The fibers containing the polymers of acrylamide have improved properties. Particularly important are the reduction in wet elongation, and sometimes of the dry elongation of the regenerated cellulose fibers, and the increase in stiffness of such fibers without embrittlement thereof. In some cases, there is an appreciable reduction of water-retention. These improved properties of the fibers and filaments impart to yarns and fabrics made from such regenerated cellulose filaments a fuller and crisper hand or feel as compared to regenerated cellulose yarns and fabrics which contain no polymers of acrylamide. They also impart to ordinary knitted or woven fabrics an improved resistance to wrinkling and to pile fabrics, when the fibers are incorporated in the pile, such as in carpets, rugs, plushes or velvets including transparent velvets, a markedly improved crush-resistance as compared to fabrics containing ordinary regenerated cellulose fibers in the pile.

The improved textile materials are produced by incorporating into the cellulosic spinning solution, such as cuprammonium cellulose solution or viscose, a polymer of an acrylamide as defined hereinbelow, at least 30% by weight of the monomeric units of which contain amide groups, extruding the spinning solution into a coagulating and/or regenerating bath, passing the coagulated and/or regenerated filament structures through customary purification procedures and drying. The purification treatments may be those usual for the particular spinning system. For example, when spinning viscose containing the polymer of an acrylamide, the filaments after coagulation or during coagulation are regenerated, such as in a dilute sulfuric acid bath, stretching being performed in conventional manner either during or after coagulation. The subsequent treatment may involve washing, desulfurization, rinsing, bleaching, rinsing, applying a soft finish and then drying. When spinning cuproammonium cellulose solutions, the usual after-treatment system may be applied after coagulation, regeneration and stretching. The drying may be effected in the normal manner, such as by passage through a tunnel drier in which heated air at about 140° F. is supplied. However, the drying or a portion of it may be effected at higher temperatures with increased effect on the properties of the filaments, yarns and fabrics mentioned hereinabove, that is, in respect to the hand, stiffness, reduction in elongation, wrinkle-resistance and crush-resistance. For example, these properties may be enhanced by including

within the drying, or by following it with, a period of heating for a duration of 3 to 30 minutes at a temperature of about 100° C. to 150° C. The improvement in the properties mentioned is obtained without this higher temperature treatment but, in many cases, the improvement in such properties is greatly enhanced when this higher temperature treatment is employed.

The term "an acrylamide" is used in the specification and claims hereof as a generic expression for the restricted class of related compounds defined in more technical fashion as follows: a mono-amide, having a single unsaturated carbon to carbon bond, of an acid of the group consisting of acrylic acid and alpha-alkyl- or beta-alkyl-substituted alpha-methylene monocarboxylic acids, and N-alkyl substituted derivatives thereof, the alkyl substituents consisting of methyl, ethyl, and both methyl and ethyl, the amide having only a single carbonyl group attached to the N atom. These acrylamides have the general formula:



in which each of R, R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen, methyl, and ethyl radicals, and may be the same or different than one or more others of the group.

The term "acrylamide polymer" or "polymer of an acrylamide" is intended to be generic to homopolymers and copolymers of the compounds just defined, whether they are produced directly by polymerization or copolymerization or indirectly by hydrolysis, saponification, or other reaction upon a previously produced polymer or copolymer. When copolymers are used, at least 30% by weight of the monomeric units in the copolymer should contain amide groups.

The polymer may be produced (1) by polymerizing or copolymerizing acrylamide itself or a substituted acrylamide (within the definition hereinabove), or (2) by hydrolyzing a polymer of copolymer of acrylonitrile or an alkyl-substituted acrylonitrile, such as methacrylonitrile, to produce a polymeric product in which at least 30% of the monomeric units comprise amido groups. The polymeric products may be produced by standard solution or emulsion polymerization techniques such as in the presence of a peroxy catalyst such as potassium persulfate.

When copolymers are used, the monomeric unit other than that containing the amide group may be, or may be considered to be derived from, any other ethylenically unsaturated monomer, such as vinyl acetate, vinyl chloride, vinyl alcohol, acrylic acid, acrylonitrile, methacrylic acid, methacrylonitrile, vinylidene chloride, ethylene, etc., or mixtures thereof. Also, in using method (2), the hydrolyzed product may contain nitrile and/or carboxyl groups as well as amido groups if it is derived from polyacrylonitrile or from polymethacrylonitrile. It may also contain other groups, such as hydroxyl and/or acetate groups if derived from copolymers, such as a copolymer of acrylonitrile and vinyl acetate.

Polymeric amides of relatively high molecular weight may be used and those polyacrylamides which, in concentrations of 10% in water containing 1% of isopropanol by weight have a specific viscosity of 300 centipoises to 6000 centipoises are preferred. The acrylamide polymers are long-chain linear substances and although they are water-dispersible at the time they are added to the viscose, and are added in the form of their water dispersions, there is no scumming of the bath or other evidence that they are leached out during spinning or after-treating. Apparently the linear structure of the polymeric amides causes them to become tangled or meshed with the cel-

lulosic chains of the viscose whereby they are restrained from being leached out by the coagulating and other aqueous baths. At the same time, their linear structure permits them to flow and align themselves with the cellulose chains during extrusion of the mixture and stretching of the article for orientation.

The textile material may contain from 1 to 15% by weight of the polymer of an acrylamide, the balance being substantially all regenerated cellulose. The preferred proportion is from 5 to 10% in pile of carpets and from 10 to 15% for ordinary fabrics for imparting improved resistance to crushing and resistance to wrinkling in the respective fabrics.

While the polymer of an acrylamide may be introduced into the viscose or cuprammonium cellulose solution at any time before spinning, it is preferred to inject the polymer into the stream of viscose as it flows to the spinnerets so as to reduce the time during which the polymer is maintained in an alkaline medium. To facilitate the introduction of the polymer into viscose, it may first be dissolved or dispersed in water. If desired, the polymer dispersions may also contain viscosity-increasing substances, such as alkaline solutions of water-soluble or water-insoluble cellulose ethers, e.g., hydroxyethyl cellulose, methyl cellulose, carbomethyl cellulose, and ethyl cellulose which have the degree of substitution and may be used in the proportions specified in my copending application Serial No. 308,296, filed September 6, 1952, now U. S. Patent No. 2,796,656, granted June 25, 1957. Other substances may be incorporated in these aqueous dispersions, such as dyes, pigments; spinning assistants for inhibiting incrustation and clogging of the spinnerets, such as lauryl pyridinium chloride, ethylene oxide condensation products of higher fatty alcohols, such as of lauryl alcohol; viscose coagulation retarders or accelerators, such as triethanolamine or diethylamine in a proportion of one to four millimoles or more than 100 grams of viscose, and so on.

The viscose used may have any spinnable composition. For example, it may be a "normal" viscose having a sodium chloride salt test value of from 3 to 6, containing from 6 to 9% cellulose, from 6 to 9% sodium hydroxide and of normal spinning viscosity, i.e., having a ball fall viscosity of 35 to 50 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. If it is desired to produce self-crimpable fibers of the type described in U.S. 2,517,694 to Merion and Sisson, viscoses and spinning baths as described in that patent may be used.

The invention is also adapted to the production of modified shaped articles, and especially filaments, by the two-bath process in which the modified viscose is extruded into a coagulating bath which effects little, if any, regeneration of the cellulose, and the article comprising cellulose xanthate is subsequently treated with a cellulose-regenerating medium, stretching of the film, filaments or the like being effected before or during the regeneration stage.

The following examples in which parts and percentages given are by weight unless otherwise stated, are illustrative of the invention. In all cases, the tests were made on the yarns after conditioning them at 58% relative humidity and 70° F. The test for water-retention is more or less standardized and involves soaking the yarns in water, centrifuging them to remove the excess water, and weighing the yarns. The difference between the weight of the conditioned yarn prior to the soaking and centrifuging and the weight of the centrifuged yarn expressed as a percentage of the conditioned weight of the yarn is a measure of the water-retention capacity of the yarn. The specific conditions under which this test is performed may vary somewhat. In the present case, the conditioned yarns were soaked for 15 minutes in distilled water at room temperature, wrapped in a cotton muslin fabric, soaked in water for an additional 15 minutes at room temperature, and then centrifuged for 3 minutes in a centrifuge having a diameter of 17 inches and rotating at a speed of 1800 r.p.m.

EXAMPLE I

A hydrolyzed polyacrylonitrile in which about 60% of the monomeric units contained carboxyl groups, about 30% contained —$CONH_2$, and the balance contained nitrile groups was introduced into a viscose containing 7.4% cellulose and 7% caustic soda so as to provide 5% hydrolyzed polymer based on the weight of cellulose. The viscose was aged to a salt point of 5.9 and spun at 60 meters per minute into a coagulating and regenerating bath containing 10% sulfuric acid, 4.5% zinc sulfate and 22% sodium sulfate maintained at a temperature of about 50° C. The filaments had a 13-inch immersion in the spinning bath. The filaments, after leaving the spinning bath, were stretched 40% between godets. After completing the regeneration, desulfurizing, bleaching and appropriately washing, one portion (hereinbelow designated A) was dried at room temperature, another portion (hereinafter designated B) was dried at 100° C. and a third portion (designated C hereinafter) was dried at 100° C. and then heated to 150° C. for 30 minutes.

The resulting groups or portions had the following properties as compared to a regenerated cellulose control yarn (containing no polyacrylamide) dried at 100° C. temperature.

Table I

	Percent Water Retention	Percent Elongation	
		Dry	Wet
Control	85.0	18.5	29.0
A	117.5	21.7	35.0
B	110.4	21.3	34.2
C	76.3	20.1	17.1

EXAMPLE II

A copolymer of 50% acrylonitrile and 50% acrylic acid was introduced into a viscose having the same composition as in Example I to provide 5% of the copolymer on the weight of the cellulose. After ageing to a salt point of 6.4, the viscose was spun into a coagulating bath of the same composition as given above. After purification of the yarns, in a manner similar to that of Example I, several portions A, B and C were dried as in Example I. The yarns had the following properties:

Table II

	Percent Water Retention	Percent Elongation	
		Dry	Wet
A	116.3	22.1	30.8
B	123.8	21.9	32.5
C	84.5	21.0	23.5

EXAMPLE III

Polyacrylamide was introduced into viscose of the same composition as in Example I to provide 10% of the polymer on the weight of the cellulose. After ageing to a salt test of 5, the viscose was spun into a coagulating and regenerating bath as in Example I maintained at a temperature of about 48° C. Portions of the yarn were purified as in Example I and dried at 100° C. (por-

tion B) and heated to 150° C. for 30 minutes after drying at 100° C. (portion C). The yarns had the following properties:

Table III

	Percent Water Retention	Percent Elongation	
		Dry	Wet
Control	85.0	18.5	29.0
B	158	16.9	23.7
C	132	17.5	22.7

EXAMPLE IV

An aqueous dispersion of polyacrylamide was injected into a stream of viscose containing 8% cellulose and 8% caustic soda aged to a salt point of 6.1 in such an amount as to supply 10 parts by weight of the polyacrylamide to 90 parts by weight of cellulose in the mixture. The mixture was spun into a coagulating bath containing 7% sulfuric acid, 1% zinc sulfate and 21% sodium sulfate at 50° C. Spinning was at 60 meters per minute and after leaving the spinning bath, the filaments were stretched 67% while being subjected to a 90° C. dilute acid bath, the size of the holes in the spinneret being selected to produce filaments having a size of 3 denier each. The filaments were cut to 2-inch staple fiber lengths and subjected to the conventional after-treatment and dried at 120° C. The fibers were highly crimped as the result of the correlation of the composition in the spinning bath with the composition of the cellulose, and stretching and relaxation after cutting in accordance with the principles of U.S. Patent 2,517,694. The dried crimped fibers were spun into yarns of the size 20/1 (cotton system). The yarns were woven into a 54 x 52 plain weave construction. After desizing, scouring and rinsing, the fabrics were dried in relaxed condition on the tenter and finished thereon as a 66 x 58 cloth count fabric. A control fabric made from regenerated cellulose fibers of the same constitution (except for the lack of the acrylamide polymer) was tested along with the acrylamide modified fabric for wrinkle-resistance. The recovery angle of the control fabric was only 116° whereas the average of two fabrics made from the acrylamide polymer containing regenerated cellulose fibers gave a recovery angle of 135°.

EXAMPLE V

Fibers were spun as in Example IV except the conditions were adjusted to produce filaments of a size corresponding to 15 denier each and they were cut to 3-inch staple lengths instead of 2-inch lengths. The polyacrylamide was injected in proportions to provide 5% by weight of polymer to 95% by weight of cellulose in one batch and 15% polyacrylamide to 85% cellulose in another batch. Yarns were made from both batches on the woolen system of a size corresponding to 1.08/2 run (woolen system). These yarns were woven as the pile into a standard Axminster 7-row 189-pitch construction. After burling, shearing, backsizing, and steaming, they were dried under conditions which included heating at 175° C. for a period of about 20 minutes. The thickness of the carpet was 0.4 inch. Fabrics made from the yarns containing 5 and 15% by weight of the polyacrylamide were tested along with a wool fabric and a fabric of regenerated cellulose made in the same way but without the introduction of an acrylamide polymer under severe service conditions, that is, by placing the carpets within

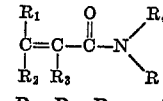
a narrow corridor through which numerous persons traveled back and forth and necessarily walked over all four carpets. The initial thickness of each carpet was the same and the thickness of the carpet was periodically tested after 4, 6 and 8 weeks of the service conditions. The measurement of the thickness of carpet at these periodic intervals was made at each of three pressures, namely, 0.1, 1.27, and 11.5 pounds per square inch. The "luxury index" was then determined for each carpet by determining the residual compression or the difference in thickness between the 1.27 and the 11.5 pound per square inch load at equilibrium crush conditions (that is, when the maximum extent of crushing as a result of service had been obtained). These residual compression values were then converted into comparative values by arbitrarily assigning the "luxury index" of 100 to wool. The higher the "luxury index," the more crush-resistant is the fiber. The following values were obtained:

Fabric:	Luxury index
Wool	100
Control	50
5% polyacrylamide	63
15% polyacrylamide	68

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. As a new article of manufacture, a crush-resistant textile comprising a regenerated cellulose fiber containing, distributed throughout the fiber, 1–15% by weight based on cellulose of a highly polymerized water-dispersible linear polymer of a monoamide of which at least 30% by weight of the monomeric units contain amide groups, said monomeric units having the general formula:



in which each of R, R_1, R_2, R_3, and R_4 are selected from the group consisting of hydrogen, methyl, and ethyl radicals, the linear structure of the polymeric amides causing them to become tangled or meshed with the cellulosic chains of the viscose whereby they are restrained from being leached out by the coagulating bath during spinning.

2. The article of claim 1 wherein the polymer is polyacrylamide.

3. The article of claim 1 wherein the polymer is a 50–50 copolymer of an acrylamide and acrylic acid.

4. The article of claim 1 wherein the polymer is a hydrolyzed polyacrylonitrile in which about 60% of the monomeric units contain carboxyl groups and about 30% contain amide groups.

5. The article of claim 1 wherein said crush-resistant textile is a pile fabric.

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