

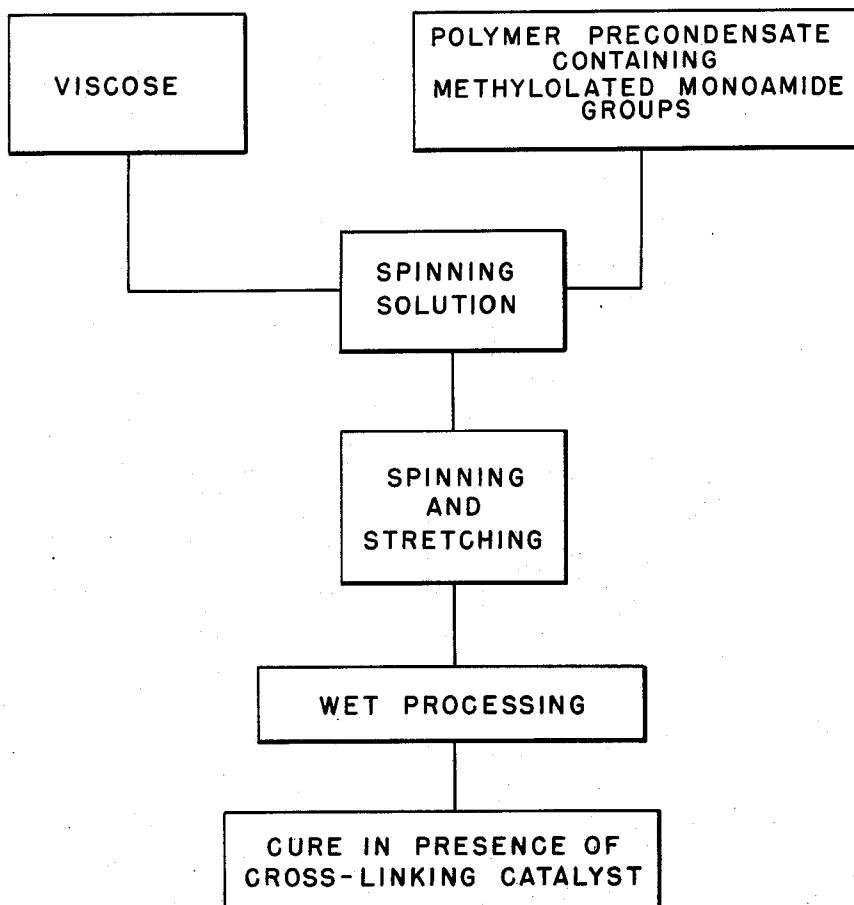
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RESIN SPUN VISCOSE

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RESIN SPUN VISCOSE

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This invention relates to fibers, yarns, fabrics and other shaped articles comprising regenerated cellulose and a heat-hardened reaction product or condensation product of a linear polymer of a monoamide and formaldehyde, which articles are characterized by markedly decreased water-sensitivity as compared to conventional regenerated cellulose articles.

This application is a continuation-in-part of U.S. Patent No. 2,858,185, issued October 28, 1958.

An important advantage of regenerated cellulose yarns is that, after initial drying thereof in the course of their production, those yarns can regain from about 7 to 11% of moisture from the atmosphere, under normal temperature and humidity conditions. This ability to regain moisture from the atmosphere is a distinct asset of the regenerated cellulose yarns and is responsible for the desirably soft "hand" or "feel" of regenerated cellulose fabrics. On the other hand, regenerated cellulose yarns are very water-sensitive and normally pick up and retain an excessive amount of water when they are exposed to water or aqueous media, the amount of water normally picked up and retained being considerably higher than 50% and up to 100% or more by weight. This is undesirable because it results in excessive swelling of the yarns with danger of distortion, the tendency of fabrics comprising the yarns to shrink progressively on repeated laundering, and protracted drying times. Also, the absorption and retention of large amounts of water by crimped regenerated cellulose fibers or yarns, as such or as they occur in fabrics, under the wet load encountered in processing the yarns or fabrics, tends to remove the crimp.

Many attempts have been made to modify regenerated cellulose textiles by after-treatment of the final dried textiles with formaldehyde or a resin convertible by heat to an insoluble condition. The after-treatment of a regenerated cellulose textile which has been purified, washed and dried involves the difficulty, among others, that the modifying agent does not readily penetrate into and through the textile and it is, therefore, difficult to obtain uniform modification of the textile throughout its cross-section. Also, in most of the after-treating methods involving the use of a resin or formaldehyde, any reduction in cross-sectional swelling of the regenerated cellulose fibers or yarns on immersion thereof in water is achieved at the expense of extensibility and complicates the textile processing.

It has been proposed to incorporate resin-forming substances in viscose or other cellulosic solutions for various purposes. For instance, it has been suggested to mix viscose with the constituents or precondensates of urea-, phenol- or melamine-formaldehyde resins and complete the condensation by heating the article formed from the mixture. However, these constituents and the precondensates of those resins are usually soluble in the spinning baths or processing liquids used in the production of yarns by the conventional viscose process and are for the most part leached out during the spinning and after-processing of the yarns. For instance, the generally available melamine-formaldehyde resin precondensates are soluble in the acid spinning baths of the viscose process, from 80 to 90% of the precondensate initially added to the viscose being lost in the spinning bath and

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other liquid treating or washing baths. Increase in the molecular weight of these partial condensates to a weight at which they cannot diffuse readily from the cellulosic structure reduces the amount of the condensate lost during the spinning to about 20% but has no effect on the tenacity and swelling capacity of the textile.

Moreover, modification of the cellulose requires a chemical reaction between the resin molecules with cross-bonding thereof and/or between the resin and the hydroxyl groups of the cellulose with the formation of cross-links between the cellulose chains. In order to effect uniform reaction between the resin molecules and/or between the resin and the hydroxyls of the cellulose, the resin should flow and align itself with the cellulose chains during extrusion of the viscose and during stretching of the yarn for orientation. Those urea-, phenol-, and melamine-formaldehyde resin precondensates which are polymerized to a stage such that they are not readily leached out of the regenerated cellulose textile are three-dimensional structures which cannot flow and align themselves with the cellulose chains but are incorporated between those chains as discrete particles. Furthermore, since these three-dimensional resin precondensates are already cross-linked structures in which most of the reactive or functional groups are "tied up" and no longer available for reaction in situ in the textile, the possibility for further cross-bonding of the resin molecules or cross-linking of the cellulose chains by the resin in or on the textile is greatly reduced.

It is an object of the present invention to provide regenerated cellulose articles of decreased water-sensitivity which pick up less water when they are immersed in water or aqueous media and therefore swell to a much less pronounced extent than conventional regenerated cellulose articles and which, on centrifuging after such immersion retain less than 50% by weight of water.

Another object is to modify the water pick-up capacity, and hence the cross-sectional swelling, of regenerated cellulose textiles, and decrease the amount of water retained by the textile after centrifuging, without impairment of the capacity of the textile to regain comparatively small amounts of moisture from the atmosphere and without any appreciable or prohibitive loss in tensile strength or elongation.

A further object is to decrease the cross-sectional swelling of regenerated cellulose textiles on immersion in water or aqueous media using a modifying polymeric material which may be added directly to viscose and which is not leached out during the spinning and processing operations.

Another object is to render regenerated cellulose textiles resistant to progressive dimensional shrinkage on repeated laundering.

A still further object of the invention is to produce regenerated cellulose articles of decreased water-sensitivity, cross-sectional swelling on immersion in water, and water-retention capacity directly from viscose having incorporated therein a resin precondensate which is in, and which remains in, reactive condition until it is converted by heat to a hardened, insoluble condition in situ on the article. Other objects will appear hereinafter.

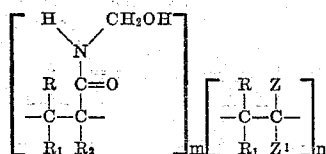
The process of this invention is illustrated in the accompanying drawing wherein the figure is a flow diagram of an embodiment of the invention.

In accordance with this invention, the water-sensitivity, cross-sectional swelling in water, and water-retention capacity of regenerated cellulose articles are decreased by bringing or converting to a heat-hardened insoluble condition in and on the articles a water-dispersible or water-soluble linear vinyl polymer, at least 50% of the units of which contain methylolated amide groups.

The term "vinyl polymer at least 50% of the units of

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which contains methylolated monoamide groups" is a generic expression covering a restricted class of rated linear polymers from the group consisting of homopolymers and interpolymers having recurring units depicted by the general formula:



wherein R, R₁ and R₂ are each either hydrogen or lower alkyl radicals (e.g. methyl, ethyl, propyl, butyl, etc.). *m* is a number from 0.5 to 1.0; Z and Z¹ are each either hydrogen (ethylene, propylene, etc.), amide, carbalkoxyl (e.g. acetate, propionate, butyrate, etc.), halogen (e.g. chlorine, bromine, etc.), hydroxyl, carboxyl, nitrile radicals or mixtures of the same, and *n* is a number from 0 to 0.5.

In other words, the vinyl polymers of this invention are ones wherein monoamide groups are attached to at least 50% of the polymeric units thereof and an average of one amido hydrogen of each such unit is replaced by a methylol group, the remainder of the polymeric units being derived from one or more of the other vinyl polymeric units defined above. The latter case not only includes interpolymers containing 1, 2, 3, 4 or more different vinyl polymeric units in addition to the amide-containing unit, it also includes a homopolymer of acrylamide, and alkyl derivatives thereof, wherein between 50% and 100% of the polymeric units have an average of one amido hydrogen per unit replaced by a methylol group.

The term "monoamide polymer" or "polymer of a monoamide" is intended to be generic to homopolymers and interpolymers of the compounds just defined, whether they are produced directly by polymerization or indirectly by hydrolysis, saponification, or other reaction upon a previously produced polymer or interpolymers.

The linear polymers of this invention, which may also be termed a reactive condensate, a partial condensate, or a precondensate, may be incorporated as such in the viscose from which the article is to be formed. This is a preferred embodiment of the invention. Such partial condensates may be produced (1) by homopolymerizing or interpolymers acrylamide itself or a substituted acrylamide (within the definition herein above) to obtain a reactive polymer at least 50% of the units of which contain amide groups, and thereafter reacting the polymer with formaldehyde, or (2) by hydrolyzing a polymer or interpolymers of acrylonitrile or an alkyl substituted acrylonitrile, such as methacrylonitrile, to produce a polymeric product in which at least 50% of the monomeric units thereof contain amido groups, and thereafter methylolating with formaldehyde. The polymeric products may be produced by standard solution or emulsion polymerization techniques in the presence of a peroxy catalyst such as potassium persulfate.

When interpolymers are used, the monomeric unit (or units) other than that containing the amide group 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 interpolymers, such as a copolymer of acrylonitrile and vinyl acetate. Condensation products of formaldehyde and the vinyl polymers of this invention pass through various stages, from water-soluble or water-dispersible reaction products which

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contain reactive amido groups having an average of at least one hydrogen on the N atom to final, heat-hardened, insoluble, condensates.

The molecular weight of the partial condensate (e.g. methylolated polyacrylamide) influences the effectiveness of the modification. When a reactive partial condensate is added to the viscose, products of relatively low molecular weight are generally most effective but they may have degrees of polymerization as high as 500 or more. For example, polyacrylamides, which, in concentrations of 10% to 20% by weight in water containing 1% of isopropanol by weight have specific viscosities between 1000 centipoises and 50,000 centipoises are suitable for methylation. Partial condensates having these or lower specific viscosities are also used if the condensate is applied to a swollen gel article.

The vinyl polymers of the present invention 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; this finding is substantiated by analysis for nitrogen on the final articles comprising the fully reacted condensate. This is apparently attributable to the linear structure of these vinyl polymers and condensates thereof which causes them to become tangled or meshed with, and restrained from leaching out by, the cellulosic chains of the viscose. 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.

Permanent modification of the moisture pick-up and retention capacity of the regenerated cellulose yarn or the like (control of the cross-sectional swelling) is obtained by bringing the reaction between the formaldehyde and monoamide polymer to completion. This is accomplished by heating the textile or other article to curing or baking temperature. It is believed that the modification of the regenerated cellulose results primarily from reaction between the molecules of the resin-condensate aligned with the cellulose chains, with the formation of bonds or bridges between the free amido groups of the condensate which bridges, or at least some of them, span the cellulose chains and serve to stabilize them, although the possibility of cross-linking of hydroxyl groups on the cellulose chains is not excluded.

The extent of reduction in water-retention, swellability and of increase in stabilization depends upon the proportion of amido groups to total monomeric units in the molecule, the larger the proportion, the greater stabilization effect and reduction in water sensitivity. The condensates containing the lower proportions of about 50% being highly useful to provide a controlled and predetermined reduction in water retention and swellability, such as is particularly desirable in the making of filter fabrics wherein a definite but limited swelling is desired to reduce the size of the interstitial spaces between the woven yarns. Condensates containing the lower proportions are also useful in the treatment of yarns produced from hollow-filament regenerated cellulose in that such treatment reduces the shrinkage of the textiles, such as fabrics, without collapsing the hollow cells. To obtain the maximum stabilization, the condensates containing higher proportions of amido groups are preferred. The condensates of polyacrylamide itself are especially preferred because of availability, low cost, and the capacity to produce a fully practical degree of stabilization of regenerated cellulose fabrics, yarns, fibers, etc. in a simple manner without the incorporation of an excessive amount of the condensate on the fabric.

The reaction between the formaldehyde and the monoamide polymer may be brought to completion by heating the regenerated cellulose article at a temperature of 100 to 170° C., preferably at 140 to 160° C. for a time

interval between 5 and 30 minutes, and preferably in the presence of an acidic catalyst. The time of reaction should generally be inversely proportional to the temperature, i.e., the higher the temperature, the shorter the time. The article comprising regenerated cellulose and the reactive partial condensate of the monoamide polymer and formaldehyde may be treated with an aqueous solution of the acidic catalyst, dried, and then heated to complete the condensation, the drying and heating being performed in two stages or a single stage. The amount of catalyst remaining on the article when it is "cured" may vary but usually when it is treated with a solution containing the catalyst in concentrations of from 0.25 to 0.50% by weight, the amount of residual acidic catalyst on the article is sufficient to catalyze the condensation of the monoamide polymer and formaldehyde.

In selecting a catalyst for use in the present process, preference is given to those catalysts which catalyze the reaction of a monoamide polymer and formaldehyde, and more highly acid catalysts which favor the reaction between formaldehyde and cellulose are preferably avoided. Any acidic catalyst which is known to catalyze urea- and melamine-formaldehyde reactions may be used. The useful catalysts may also be described as those water-soluble acids and acid salts which, in concentrations of 0.25 to 0.50% by weight in water, form aqueous solutions having a pH between 1.0 and 4, or which, on heating, dissociate to evolve a volatile base, leaving an acidic residue. Highly acid catalysts which in aqueous solution have a pH lower than 2.5 such as sulfuric acid, are preferably avoided so as to minimize direct reaction of the formaldehyde with the cellulose and also to avoid degradation of the cellulose. Examples of preferred catalysts are ammonium chloride, monobasic ammonium phosphate, monobasic sodium sulfate, magnesium chloride (usually the hexahydrate), dibasic ammonium phosphate, monobasic ammonium sulfate, lactic, citric, tartaric, oxalic, formic, propionic, boric, or succinic acids, or a combination of sodium chloride (2.0 to 10%) and tartaric acid (0.1 to 1.0%).

The textile or the like comprising the residual acidic catalyst may be heated to "curing" temperature at any stage after its production. Thus, yarns may be initially dried and then heated for "curing" or initially dried yarns may be woven, knitted or otherwise formed into fabrics and then heated to the "curing" temperature. If the yarns are in crimped condition, it is preferred to complete the condensation of the formaldehyde and the monoamide polymer after the yarns have been spun, processed and dried in relaxed condition. The heating is performed on the relaxed yarns to set the crimp and to preserve it during working up of the yarns. In other cases, it may be preferable to complete the condensation after the yarns are fabricated or during finishing of the fabrics. Fabrics comprising the regenerated cellulose yarns having the formaldehyde monoamide polymer condensate distributed throughout their cross-section in the final heat-hardened, insoluble condition, are stabilized against progressive dimensional shrinkage on repeated laundering.

The viscose used 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% cellulose, from 6 to 9% sodium hydroxide and of normal spinning viscosity, i.e., having a ball fall viscosity of 35 seconds at 18° C.

The regenerated cellulose article may contain from 1 to 25% or more by weight (based on the weight of the cellulose in the viscose) of the formaldehyde-monoamide polymer condensate. Optimum results are obtained with about 3 to 10% of the condensate derived from polyacrylamide itself (3 to 5% when fully methylolated). When the polymer contains only 50 to 70% of reactive amido-containing monomeric units, a proportion of 13

to 20% is preferred if a large reduction in the water-retention and so forth is desired.

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, spinning baths as described in that patent may be used. That patent points out that a spinning bath of the type just mentioned has, because of its high salt content, a rapid dehydrating action on the extruded filaments and sets up thereon an at least partially regenerated skin of substantial thickness around a still liquid or soft plastic core. This skin is set up rapidly and because of the dehydrating action of the coagulating bath has a strong tendency to shrink circumferentially so as to reduce the filament diameter. But this force is overcome by the incompressible core, whereupon the skin ruptures longitudinally along the filament, permitting part of the core to flow through the rupture. In this state the filaments are finally set up. That portion of the resulting filaments which was forced out of the core responds to subsequent stretching differently from the remainder of the filaments, as if it had originated from a different viscose. One portion of the cross-section has a thick skin showing a break along its juncture with the other portion which has a thin skin or none at all. In the crimped filaments the portion having the thick skin always takes the inside of the bends of the crimp, because of a stronger tendency to shrink. The crimped filament takes the form of a regular or irregular helical coil.

The invention is also adapted to the production of modified shaped articles 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.

The formaldehyde-vinyl monoamide polymer condensate may be added to the viscose at any time but in order to avoid hydrolysis of the amide or changes in the ageing or ripening cycle for the viscose it is preferred to mix the aqueous dispersion of the modifier with the viscose after the latter has reached the predetermined spinning age, for instance by injecting the aqueous dispersion of the formaldehyde precondensate of the vinyl monoamide polymer into the viscose as it is extruded through the spinneret or other forming device.

The following examples in which parts and percentages given are by weight unless otherwise stated, are illustrative of the process of the invention. These examples include tables showing the results obtained when the modified textiles were tested for water-retention, tenacity, and elongation. In all cases, the yarns obtained by the procedures described were weighed and conditioned at 58% relative humidity and 70° F., prior to being tested. 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 yarns prior to the soaking and centrifuging and the weight of the centrifuged yarns is a measure of the water-retention capacity of the yarns. 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" and rotating at a speed of 1800 r.p.m. The

results obtained by testing the water-retention capacity of the yarns by methods involving modifications of the soaking time and temperature, the centrifuging time, and the speed at which the centrifuge is rotated bear the same relationship as the values obtained under our conditions.

In the tables included in the examples, the modified yarns are compared to control yarns of regenerated cellulose which did not contain the monoamide-formaldehyde condensate but which had been conditioned for testing in the same manner as the modified yarn.

Example 1

Molar proportions of formalin and polyacrylamide having a specific viscosity of 3200 centipoises at 10% solids concentration in water containing 1% isopropanol are mixed and the pH of the mixture adjusted to about 9.5. This mixture is then heated at a temperature of about 50° C. for about two hours producing a reactive partial condensate of formaldehyde and polyacrylamide which at a solids concentration of 10% in water containing 1% isopropanol has a specific viscosity of 40 centipoises. This reactive condensate was added to viscose in such quantity that the viscose contained 10% of the reactive condensate based on the weight of the cellulose in the viscose. The viscose was one of normal viscosity containing 7% cellulose and 7% sodium hydroxide, and it had been aged to a sodium chloride salt test value of 5. This mixture of viscose and the reactive condensate was spun into an aqueous coagulating and regenerating bath containing 10% sulfuric acid, 4.5% zinc sulfate, and 24% sodium sulfate at about 45° C. The filaments thus formed

EXAMPLES 2 THROUGH 5

The procedure for methylation, spinning and condensation described in Example 1 was repeated producing a series of methylol polyacrylamides having the specifications shown in Table II, with the exception that the sodium sulfate content of the coagulating and regenerating bath was 22%, the bath temperature was 50° C., monobasic ammonium phosphate at 0.25% concentration was substituted as the catalyst, the yarns were dried by centrifuging, and then heated at 100° C. for 20 minutes.

Table II

Example No.	Percent Organic Solids	Viscosity, cps.	pH	HCHO		Percent Methylation
				Free	Combined	
2	15	87,000	6.9	0.3	0.5	15
3	15	58,000	7.1	0.4	1.3	30
4	15	700	6.8	1.1	3.3	100
5	20	5,000	7.8	1.2	4.5	100

In addition to spinning the reactive condensate at 10%, yarns were also produced which contained both reactive condensates at concentrations of 12.5 and 15%. Additional spinings were made at the 12.5% resin concentration adding formalin to the reactive condensate in concentrations of 0.5, 1.0, 2.0 and 4.0% based on the reactive condensate solids. The treated yarns were tested for swelling by the water retention method, tensile properties and nitrogen content, the results of which are shown in Table III.

Table III

Example	Percent HCHO Added	Percent Resin	Percent Water Retention	Tensile Strength		Percent Elongation		Percent Elongation Dry at 2.00 gm./den.	Percent N
				Dry	Wet	Dry	Wet		
2	2	10	74.5	2.3	1.2	18.3	26.6	14.7	1.25
		12.5	75	2.2	1.3	17.5	24.9	15	1.86
		15	73	2.3	1.2	17.8	23.9	17.7	2.19
		12.5	64	2.2	1.2	16.7	18.9	15	1.12
		10	67	2.2	1.3	18.3	24.0	15.5	1.43
3	0.5	12.5	61.5	2.3	1.3	17.0	19.2	13.5	1.86
		15	59	2.3	1.2	17.2	19.0	14	2.18
		12.5	47	2.2	1.2	14.7	15.1	12.7	1.77
		1.0	48	2.2	1.2	14.4	14.7	12.3	1.83
		2.0	43	2.2	1.2	14.1	14.0	12.3	1.77
4	4.0	12.5	42	2.2	1.2	12.3	11.7	11	1.68
		10	43.5	2.1	1.1	12.2	10.0	10.7	1.71
		12.5	47	2.2	1.2	16.7	17.5	14.5	1.95
		15	38.5	2.2	1.2	11.2	10.3	10	2.31
		12.5	47	2.3	1.2	15.1	15.4	12.5	1.08
5	1.0	12.5	46	2.2	1.2	13.3	14.3	12	1.13
		12.5	42	2.2	1.2	12.4	12.6	10.7	1.47
		4.0	40	2.2	1.2	12.2	11.8	10.7	1.44
		10	47.9	2.2	1.1	14.0	13.9	13.0	1.11
		12.5	47.8	2.2	1.2	12.4	12.6	11.8	1.66
5	15	12.5	41.9	2.2	1.2	12.5	12.4	11.2	1.94
		12.5	50.0	2.2	1.1	14.3	13.5	13.0	1.51
		1.0	41.7	2.3	1.2	13.1	12.1	11.0	1.68
		2.0	41.5	2.2	1.2	11.0	11.0	9.8	1.96
		4.0	43.0	2.2	1.2	14.1	14.8	12.5	1.49

were given a 13-inch immersion in the bath, withdrawn, and stretched about 40% between godets to produce a 150 denier, 40 filament yarn which was washed free of spinning bath, after which it was soaked in 0.25% dibasic ammonium phosphate for five minutes and dried. It was then heated at 150° C. for 30 minutes to complete the condensation of the reactive partial condensate. These yarns (A in Table I) were then scoured, dried and tested for water retention with the results in Table I.

Table I

	Percent Water Retention	Tenacity, g./denier		Elongation at break, percent	
		Dry	Wet	Wet	Dry
Control	85.0	2.3	1.2	18.5	29.0
A	44.5	2.2	1.3	12.7	12.9

It can be concluded from the preceding examples, particularly Examples 2 through 5, that the degree of cellulose modification is directly related to the concentration of the methylol polyacrylamide (reactive partial condensate). The reduction in water retention and elongation properties demonstrates this conclusion. Highly methylolated polyacrylamide is most effective in modifying the properties of the rayon fiber. As will be observed, the order of reactivity of the reactive condensates followed the order of methylation.

The reactive condensates of Examples 4 and 5 are described as being 100% methylolated, but the combined formaldehyde values are 3.3 and 4.5% respectively, and on the basis of the calculated total acrylamide, this represents methylation of 3 out of 4 amido groups. On the other hand, the free formaldehyde plus the combined formaldehyde will account for sufficient formaldehyde to permit 100% methylation.

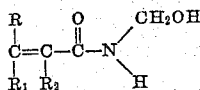
The reactive condensates of Examples 4 and 5 are

identical in formaldehyde content but vary in viscosity, the resin of Example 4 being a derivative of a high viscosity polyacrylamide and that of Example 5 being a derivative of a medium viscosity polyacrylamide. Since a comparison of fiber properties shows no really significant difference, it can be concluded that the viscosity of the reactive partial condensate, and the polyacrylamides from which they are derived, within the limits of these examples, is of no importance.

Table III also illustrates that the addition of formaldehyde to the reactive partial condensate solutions prior to injection spinning is effective in increasing the reactivity of the reactive partial condensates, particularly for reactive condensates with lower initial degrees of methylation. In the experiments tabulated, formaldehyde additions varied from 0.5 to 4.0%, this upper value being equivalent to a fully methylolated acrylamide.

I claim:

1. A method which comprises mixing viscose with an aqueous dispersion of a resinous linear polymer at least 50% of the units of which are derived from an amide having the formula:



wherein each of R, R₁ and R₂ is a radical selected from the group consisting of hydrogen and lower alkyl radicals, shaping and coagulating the mixture to form a shaped article, regenerating cellulose in the article and then heating the article to cure the said resinous polymer.

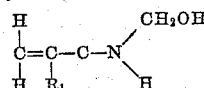
2. The method of claim 1 wherein said resinous linear polymer is polyacrylamide wherein at least 50% of the amide groups have an average of one hydrogen per amide group replaced by a methylol group.

3. The method of claim 1 wherein said heating step is conducted at a temperature of between about 100 and 170° C. for 5 to 30 minutes in the presence of an acidic catalyst.

4. The method of claim 3 wherein said resinous linear polymer is polyacrylamide wherein at least 50% of the amide groups have an average of one hydrogen per amide group replaced by a methylol group.

5. The method of claim 1 further characterized in that said mixture of viscose and said resinous linear polymer is spun into an aqueous coagulating bath containing about 7 to about 13.5% sulfuric acid, about 18 to about 28% of an alkali metal sulfate and about 0.1 to about 5% zinc sulfate, recovering a plurality of filaments from said spinning bath, stretching and washing said filaments, crimping said washed and stretched filaments by soaking them in a relaxed condition in an aqueous solution containing an acidic cross-linking catalyst, drying and heating the crimped fibers in a relaxed condition to effect cross-linking of said resinous linear polymer.

6. A method of producing regenerated cellulose shaped articles having a decreased water retention which comprises mixing viscose with an aqueous dispersion of a resinous linear polymer of an amide having the formula



25 wherein R₁ is a radical selected from the group consisting of hydrogen and methyl, shaping and coagulating the mixture to form a shaped article, regenerating cellulose in the article, and then heating the article to cure the said resinous polymer.

References Cited in the file of this patent

UNITED STATES PATENTS

2,155,067	Ubbelohde	Apr. 18, 1939
2,173,005	Strain	Sept. 12, 1939
2,297,746	Charch	Oct. 6, 1942
2,322,981	Ubbelohde	June 29, 1943
2,447,621	Smidth	Aug. 24, 1948
2,510,762	Simons	June 6, 1950
2,572,936	Kulp et al.	Oct. 30, 1951
2,796,656	Schappel	June 25, 1957