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3,218,792

## CELLULOSIC TEXTILE MATERIAL

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This is a continuation-in-part of my copending application Serial No. 684,852, filed September 19, 1957, and now abandoned.

This invention relates to a cellulosic textile material and more particularly to an improved yarn comprising both cotton and regenerated cellulose.

Recently, there has been widespread use of yarns having fibers of two or more types, and mixtures of cotton and regenerated cellulose have been considered.

Various desirable qualities have been theoretically possible with such a blend. Thus, for example, cleaner, smoother and more regular fabrics would appear obtainable since regenerated cellulose fibers process more satisfactorily in textile machinery than cotton. Moreover, since regenerated cellulose fibers can be made in various deniers, special yarns can be made after admixture with cotton, which would not be possible with cotton alone. Special handling and draping effects can be obtained with mixtures of cotton and regenerated cellulose fibers. In addition, certain regenerated cellulose-cotton blends have been reported to have superior wear resistance to pure cotton in actual use.

Despite these potentially attractive features, yarns of cotton and regenerated cellulose have had disadvantages because of certain fundamental differences in the properties of these two types of fibers.

It is well known, for instance, that the extensibility of regenerated cellulose is considerably greater than the extensibility of cotton and therefore a simple combination of these fibers in a yarn results in the cotton fibers taking substantially all the stress with a corresponding reduction in tensile strength. Again, while it is desirable to mercerize cotton, regenerated cellulose fibers cannot withstand the mercerization treatment ordinarily given to cotton fiber. Because of these and other differences in properties, the combinations of cotton and regenerated cellulose considered practical prior to this invention were very low in regenerated cellulose content.

It is a primary object of this invention to provide a yarn comprising both cotton and regenerated cellulose fibers in which the regenerated cellulose fibers have properties similar in many respects to cotton fibers.

A further object of this invention is to provide a yarn of the class described which when processed into fabric can be subjected to mercerization and pre-shrinking treatments normally given to cotton fabric.

It has now been found these and other objects may be accomplished by means of a yarn consisting essentially of untreated cotton fibers and regenerated cellulose fibers which have been cross-linked.

The term "untreated cotton fiber," as used herein, is intended to mean cotton fibers which have not been treated with a cross-linking agent. However, it includes cotton fibers which have been subjected to non-reactive sizes, lubricants, mercerization, preshrinking treatments, or other similar treatments or reagents conventional in the processing of cotton fibers.

The term "regenerated cellulose" is used in the present application, in the sense ordinarily used in the textile art, and includes regenerated cellulose made by any of the conventional techniques, i.e. by the viscose, cuprammonium or nitrate processes. However, it is preferred to use regenerated cellulose which has been made by the viscose process.

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The invention is applicable to all forms of fibrous regenerated cellulose, to both staple and continuous filament fibers. However, it is of particular importance in the treatment of staple fiber.

"Cross-linked" regenerated cellulose fibers are fibers in which adjacent cellulose chains are linked together at one or more points along their length. Numerous reagents are known which will effect this cross-linking. Any of these may be used in the present invention. Thus regenerated cellulose fiber used in the invention may be cross-linked, for example, by heat hardenable resinous materials, including the so-called reactant type resinous materials, formaldehyde, and various polyaldehydes and hydroxyaldehydes.

Suitable heat hardenable resinous materials include the aminoplasts, which may be defined as heat hardenable resinous compositions which are the condensation products of compounds having at least two amino hydrogens, with methylol forming compounds. Typical aminoplasts are urea-formaldehyde, melamine-formaldehyde, dicyandiamide-formaldehyde, guanidine-formaldehyde and combinations of these. The term is also used to include the methylol amino-epihalohydrin compounds described in United States Patent No. 2,960,464 to George C. Daul.

The term is also used to include modified urea resins, i.e. methylol compounds such as methylated methylol urea, partially polymerized methylated methylol urea, methylated and unmethylated methylol ethylene ureas such as dimethylol ethylene urea, and methylated and unmethylated methylol 1,2-propylene ureas as well as dimethylol triazines, triazones and the like. These are the so-called reactant type resins, which are heat hardenable, but which for the most part remain water soluble under the conditions required for cross-linking.

Other resins which are suitable for use in the present invention are those formed by the reaction of formaldehyde and acrolein as described in United States Patent No. 2,696,477; resins formed by the reaction of acetone and formaldehyde as described in United States Patents Nos. 2,504,835 and 2,711,971; and polyepoxy resins, e.g. polyfunctional compounds having at least two epoxy groups linked through a hydrocarbon, polyhydric phenol or polyhydric alcohol group, such as the resins formed from saturated polyglycidyl ethers of polyhydric alcohols as described in United States Patent No. 2,752,269. Particularly useful compounds of the last named class are the condensation products of epichlorohydrin with ethylene glycols.

Cross-linking agents commonly used in the industry also include formaldehyde, dialdehydes such as glutaraldehyde and adipaldehyde; mixed aldehydes such as acrolein; glycidyl aldehydes; polyacetals (including diacetals of polyhydroxy compounds as described for example in United States Patent No. 2,786,081) divinyl sulfone; dihalohydrins, for example, dichlorohydrin; and di- and tri-aziridinyl phosphine oxides and sulfides such as are described in United States Patent No. 2,859,134.

It will be understood that the exact composition of the cross-linking material used is not a part of the present invention, and other cross-linking agents used in the textile industry may be employed as desired.

The conditions under which the cross-linking agents are applied will vary with the type of agent. Resinous materials are preferably applied while they are in a state such that they will form aqueous solutions or stable dispersions containing at least 5% by weight resinous material and such that the molecular size of the material is sufficiently small to enable the resin molecules to penetrate into the interior of the fiber. In general it is preferred to apply the resinous material while it is in a substantially precondensed, monomeric or low polymer state, with a molecular weight on the order of 100-1000, pref-

erably less than about 600. The extent of polymerization which is permissible will depend on the type of resin being employed and as will be brought out more fully below, on the condition of the fiber at the time it is treated.

In effecting cross-linking the regenerated cellulose fiber is preferably treated while still in the never-dried gel state after spinning. In this way the fiber absorbs the cross-linking agent far more readily, permitting a more thorough penetration of the material into the fiber. In particular the technique described by G. C. Daul et al. in their Patent No. 2,902,391 and its continuation-in-part application Serial No. 819,465, filed June 10, 1959, now Patent No. 3,038,777, may advantageously be used. In employing this technique the fiber, while still in the gel state after spinning and before it has ever been dried sufficiently to convert it from the gel state, is treated with liquid containing the cross-linking agent and squeezed or otherwise processed until its liquid content (based on the weight of oven-dried impregnated fiber) is less than the water imbibition of the fiber in the gel state. The technique described is especially valuable in insuring that all the agent will be carried into the interior of the fibers.

The temperature of the liquid containing the cross-linking agent used to treat the fiber is not a critical factor and will vary with the particular agent being applied. Normally it will be between about 15° C. and about 50° C., preferably between about 20° C. and about 40° C.

The concentration of cross-linking agent in the aqueous impregnating liquid will again vary with the particular agent and with the type of fiber treated. Usually it will be between about 0.5 and about 15% by weight of the liquid.

The bath may contain various ingredients other than the cross-linking agent or its components. For example, it may contain a catalyst to aid in curing the cross-linking agent. Obviously the type of catalyst will depend on the particular agent being used.

When the cross-linking agent is formaldehyde a metallic salt which is a Lewis acid in the solid state is preferably used as the catalyst in accordance with the teaching of copending application Serial No. 81,956 of G. C. Daul et al., filed January 11, 1961, now Patent No. 3,113,826. In accordance with the teachings of that application, the amount of catalyst or curing agent used is between about 0.003 and about 0.09 mols per 100 g. of cellulose, normally equivalent to concentrations of from about 0.03 to about 0.9 mols/liter. The formaldehyde concentration is such as to furnish from 0.1 to 3% formaldehyde bound to the cellulose. This may be economically furnished by concentrations of 0.5 to 6%, though higher concentrations may be used.

When a resinous cross-linking agent is used the solution may contain from say 5 to 15% of the resinous material, together with say 2 to 20% on the weight of the resin of a catalyst.

The liquid may also contain wetting agents to aid in penetration of the fiber by the cross-linking agent, as well as from 0.2 to 4% on the weight of the liquid, of a finishing agent to add lubricity, cohesion, water repellancy, scroop or other desired properties to the fiber. Materials well known to the art such as polyglycol stearate, lauryl ketene dimer, silicone emulsions, stearamido methyl pyridinium chloride, octadecyl pyridinium sulfate and others may be used alone or in combination for this purpose.

The regenerated cellulose fiber may be treated as staple fiber or as tow in the manner disclosed, for example, in the copending application of Rowell et al. Serial No. 636,420, filed February 11, 1957, now forfeited, and its continuation-in-part Serial No. 143,093, filed October 5, 1961, now Patent No. 3,173,752 and then cut up into staple.

In making yarns according to the invention, fibers of

cotton and cross-linked regenerated cellulose preferably in proportions ranging from 30-70 to 70-30 are blended before spinning on conventional machinery. However, the invention is valuable for blends containing down to about 10% treated regenerated cellulose.

As an illustration of the process of blending the fibers to make yarn in accordance with this invention, cotton fibers are loosened up from the bale and prepared for feeding into the pickers. The picker room generally contains a number of pickers in which the cotton is opened up so that sand, neps, leaves, and dust may be eliminated, and to form the lint into an increasingly even and filmy lap. Preferably the treated regenerated cellulose fibers are added while the cotton fibers are being processed in the picker although they may be added at any time before the final stage or finishing picker so that a uniformly-blended lap is provided before entry into the carder.

In the carder, the cotton fibers are further cleaned and all of the fibers in the blend are laid substantially parallel. The thin band of blended fiber containing cotton and resin-treated regenerated cellulose is then reduced to a narrow sliver by being passed through an eye or other methods conventional in the art. If desired, the carding process may be repeated to provide fine yarns known as "doubly-carded" yarn. In addition, the fibers may be combed when a very fine grade of yarn is desired.

After carding, the yarn is subjected to a drawing process which is usually repeated about three times. In this stage of the process several slivers are united and drawn together thereby removing weak points and providing even, smooth slivers. The slivers are also doubled many times during the drawing and generally receive some twist in order to prevent breakage. Slubbing may be done by a bobbin and fly-frames in which the first twist is put onto the yarn. The yarn proceeds through a series of machines in which the attenuated slivers or soft yarns are united so that as the processing proceeds a finer and more twisted yarn is provided. The final frame makes the roving which is the last step before spinning.

The spinning of the blended fibers of this invention may be done by any of the known methods and machines such as the upright frame, by the flyer or ring system, or by the mule. The actual processing involved depends upon the size and quality of the yarn desired.

The blended yarn may be given various finishing treatments such as bleaching, mercerizing, dyeing, and sizing, in accordance with procedures well-known in the cotton industry, without any adverse effect on the regenerated cellulose fibers. In fact, blended yarn made in accordance with the invention is superior to blends of cotton and untreated rayon in its acceptance of many finishes, e.g. in its ability to take further cross-linking treatments. Thus if a yarn of untreated cotton and rayon is treated with a cross-linking agent, the rayon will pick up so much more agent than the cotton that it tends to become over-treated with loss of physical properties. When, however, cross-linked rayon is blended with cotton and the resulting yarn is further treated with cross-linking agent the pick up is more nearly the same and an evenly treated final product can be obtained.

The invention will be further described by means of the following specific examples, it being understood these examples are given for purposes of illustration only and are not to be taken as in any way limiting the invention beyond the scope of the appended claims.

#### EXAMPLE 1

A melamine-urea-epichlorohydrin-formaldehyde pre-condensate is prepared as follows:

Sixty grams (1 M) urea are reacted with 56 ml. (0.7 M) of epichlorohydrin in the presence of 50 ml. of water at reflux. When the temperature reaches 108° C.,

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heating is discontinued and 88.2 g. melamine (0.7 M) are added with stirring, and heating is resumed. 80 ml. (1 M) epichlorohydrin are added dropwise while maintaining reflux conditions. Heating is continued for fifteen minutes after the final addition of epichlorohydrin.

Vacuum is then applied and 22 ml. of water and 3 ml. unreacted epichlorohydrin are removed. The product is allowed to cool to room temperature (25° C.) and 20 ml. of 25% sodium hydroxide solution are added and mixed well.

4.5 moles of formaldehyde are then mixed with sodium hydroxide, added to the product above and the mixture is heated with stirring to 74° C. The clear precondensate solution is then filtered and allowed to stand for twenty-four hours.

Staple viscose fibers having a length of from 1½ to 1⅞ inches are treated with the resinous material, prepared as above, by the procedure described in Patent No. 2,902,391 and mixed in various proportions with precarded American Upland cotton, middling grade, having an average length of 1⅞ inches. These blends are spun into 20/1 yarns using a range of twist multipliers. For comparison, yarns composed of similar blends of untreated viscose rayon fibers having the same staple length are also spun. Tests are conducted for these samples and also for yarns consisting of 100% rayon, 100% treated rayon and 100% cotton.

The comparative strength relationships of the yarns are shown in the table below. Figures are for the break factor of single strand and skeins of 20/1 yarn having the specified proportions of cotton fiber, untreated rayon (UR) and treated (cross-linked) rayon (TR).

Table  
YARN BREAK FACTORS<sup>1</sup>

Twist Mult.	100% Cotton	¾ Cotton, ¼ UR	¾ Cotton, ¼ TR	½ Cotton, ½ UR	½ Cotton, ½ TR	¼ Cotton, ¾ UR	¼ Cotton, ¾ TR	100% UR	100% TR
3.0.....	224	190	200	172	180	215	212	270	236
3.5.....	245	193	213	187	220	220	226	255	250
4.0.....	255	205	228	190	230	215	224	242	270
4.5.....	265	223	234	198	230	204	213	234	260
5.0.....	253	245	235	197	231	179	210	227	227

SKEIN<sup>2</sup>

	2,008	1,616	1,800	1,605	1,883	1,886	1,754	2,316	2,055
3.0.....	2,125	1,790	1,960	1,680	1,980	1,867	1,965	2,262	2,166
3.5.....	2,338	1,885	1,990	1,690	2,010	1,860	1,975	2,187	2,155
4.0.....	2,319	1,925	1,965	1,696	2,025	1,812	1,980	2,093	2,115
4.5.....	2,270	1,925	1,865	1,655	1,950	1,714	1,884	2,017	1,920

<sup>1</sup> Break factor is the breaking force in ounces for a given yarn multiplied by the cotton count of that yarn.

<sup>2</sup> Skein breaking load is measured on a 120 yarn skein of 1.5 yards circumference. Skein break factor is breaking load in pounds multiplied by the cotton count of the yarn.

The table above illustrates that the yarns composed of treated rayon and cotton fibers have improved strength characteristics over the untreated rayon cotton blend, and the advantages are particularly evident for 50-50 blends.

The improved strength characteristics of the treated rayon cotton blend are also apparent in wet strength tests, and this is believed due to the lower water absorption of the treated rayon fiber. For example, 50-50 blends of cotton and untreated rayon at optimum twist multipliers showed a break factor of 198 (dry) and 170 (wet) whereas 50-50 blends of cotton and treated rayon at optimum twist multiplier showed a break factor of 230 (dry) and 225 (wet). Advantages are also found in yarn evenness of the treated rayon-cotton blends in comparison to the untreated rayon-cotton blend.

#### EXAMPLE 2

The procedure of Example 1 is followed except that the treated rayon used is prepared by treating a blanket of textile grade rayon staple fiber still in the gel state with a liquid bath containing 5% by weight of an acrolein-formaldehyde precondensate (1 mol acrolein:4 mols formaldehyde), 5% of a urea formaldehyde precon-

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densate (1 mol urea:1.6 mol formaldehyde), 0.75% magnesium chloride hexahydrate (catalyst) and 0.15% of a lauryl ketene dimer and 0.15% polyglycol stearate (finishing agents). The impregnated fiber blanket is then squeezed sufficiently to reduce the liquid content to 90% of the weight of the cellulose. The blanket is then opened, dried and cured as before.

The treated fiber has a water imbibition value of 44% and is combined with staple cotton fibers and spun into yarns comprising ⅓ treated rayon and ⅔ cotton, ½ treated rayon and ½ cotton, and ⅔ treated rayon and ⅓ cotton.

#### EXAMPLE 3

The procedure of Example 2 is repeated wherein the treating bath contains 15% of an acetone-formaldehyde precondensate (1 mol acetone:4 mol formaldehyde), 4% sodium carbonate (catalyst), and 0.15% lauryl ketene dimer, 0.15% polyglycol stearate (finishing agents). A yarn having improved properties over simple rayon-cotton blends is obtained.

#### EXAMPLE 4

The procedure of Example 2 is repeated wherein the treating bath contains 12% of a polyepoxy-polyglycol precondensate (Eponite 100), 1.5% zinc fluoroborate (catalyst), 0.6% polyvinyl alcohol (emulsifier) and 0.15% epoxidized soyabean oil (finishing agent). In this case the fiber blanket is squeezed to retain 85% of the weight of the liquid on the cellulose, or 60 percentage points below the gel water imbibition of the fiber (145%). Similarly good results are obtained.

#### EXAMPLE 5

Regenerated cellulose staple fiber still in the gel state after spinning is impregnated with an aqueous solution containing 1.0% HCHO and 2.0% MgCl<sub>2</sub>·6H<sub>2</sub>O, squeezed to 100% pickup, dried at 105° C. and cured at 150° C. for 12 minutes. The fiber has a water imbibition of 55%.

The treated staple having an average length of 1½" is then blended with its own weight of precarded American Upland cotton, middling grade, having an average length of 1¼ inches. The yarns are then immersed in 18% caustic soda at 18° C. for 2 minutes (normal cotton mercerizing conditions). After drying they are tested for dry tenacity and it is found that their tenacity is about 108% of the untreated blend. An identical blend of the same rayon, not cross-linked, with the same cotton retains only 94% of its tenacity after the caustic treatment.

From a consideration of the foregoing it will be seen that the present invention provides a new type of yarn having both cotton and regenerated cellulose components which overcomes the difficulties previously experienced in blending these two materials. By cross-linking, the regenerated cellulose component is given many properties

approaching those of cotton, while retaining the desirable characteristics inherent to it. Fabrics made from the yarn are remarkably regular in texture. They can be mercerized in the same manner as all cotton fabrics and they dye evenly with the dyestuffs usually used for cotton. Moreover, by treating only the regenerated cellulose component the total quantity of cross-linking agent employed in the yarn taken as a whole is kept to a minimum, which is advantageous from a cost standpoint and also avoids the decrease in tear strength of fabrics made therefrom, which often accompanies a high degree of cross-linking.

In addition to the advantages set forth above, exceptionally good results are found when fabrics made from the yarn of this invention are to be given additional cross-linking treatments designed to give dimensional stability, handle, wash and wear properties and crease resistance. When cross-linking treatments are applied to fabrics made from mixtures of cotton and untreated regenerated cellulose fiber, the fabrics tend to lack stability and show reduced crease resistance compared to resin treated all cotton fabrics. On the other hand, fabrics formed from the yarn of this invention accept further cross-linking treatments evenly since (a) the swelling of the treated viscose cross-linked staple is close to that of cotton and resin acceptance is controlled and (b) the stability of the treated viscose staple is very high.

What is claimed is:

1. A yarn consisting essentially of from 30-70% by weight untreated cotton fibers, and from 70-30% by weight cross-linked regenerated cellulose fibers.

2. The yarn claimed in claim 1 wherein the regenerated cellulose fibers are cross-linked by means of a heat-hardened resin.

3. The yarn claimed in claim 1 wherein the regenerated cellulose fibers are cross-linked by means of formaldehyde.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

1,785,823	12/1930	Thoma	161-173
2,078,886	4/1937	Weinberg	57-140
2,252,999	8/1941	Wallach	57-140
2,254,881	9/1941	Bell	57-140
2,261,556	11/1941	Marsh et al.	161-259
2,271,184	1/1942	Dreyfus	57-140
2,289,039	7/1942	Reichel	8-120
2,327,760	8/1943	Bestian	117-139.4
2,902,391	9/1959	Daul et al.	117-145
2,955,014	10/1960	Segal et al.	8-120 X
3,039,167	6/1962	Lund	26-19

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