

Aug. 28, 1962

R. WOODELL

3,050,823

CRIMPABLE REGENERATED CELLULOSE FIBERS AND YARN

Filed Oct. 30, 1958

Fig. 2

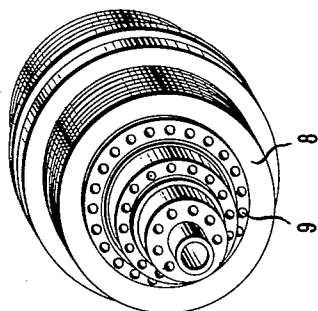


Fig. 1

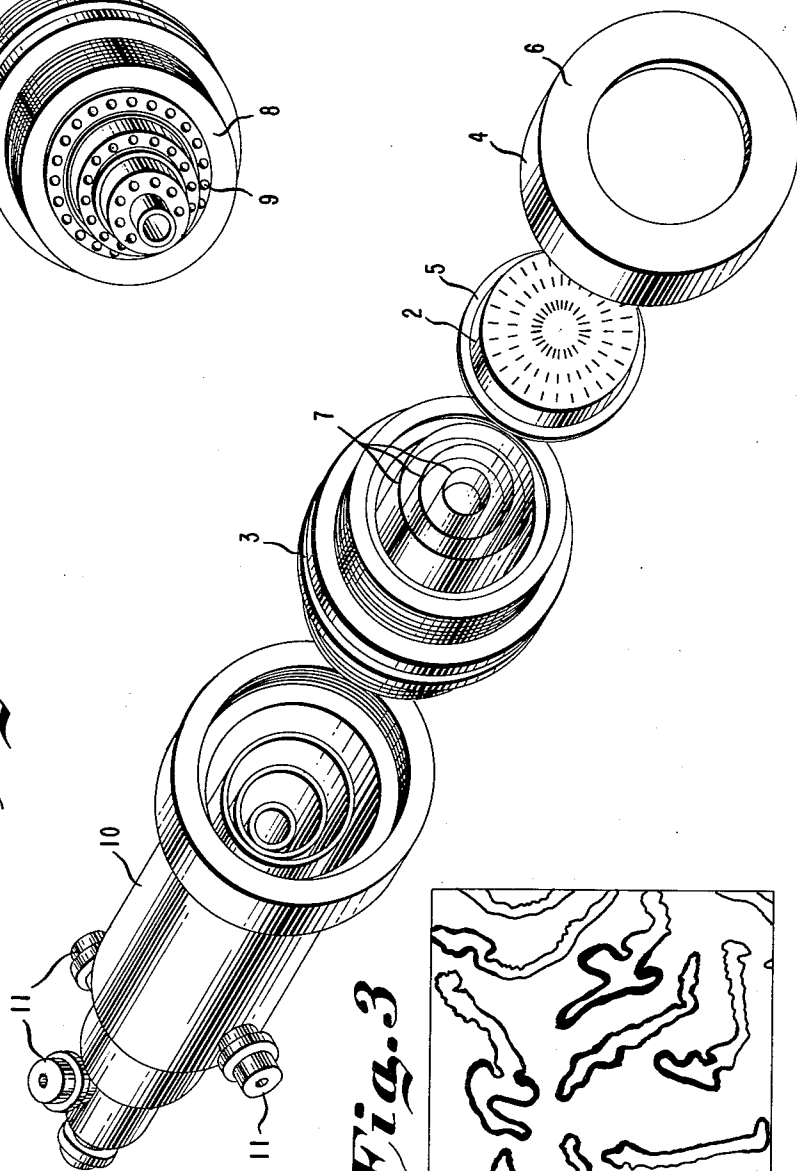
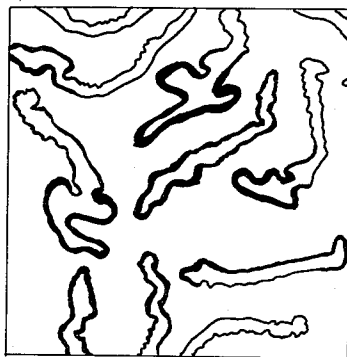


Fig. 3



INVENTOR

RUDLOPH WOODELL

BY *Francis H. Deaf*
ATTORNEY

1

3,050,823

CRIMPABLE REGENERATED CELLULOSE FIBERS AND YARN

Rudolph Woodell, Kinston, N.C., assignor, by mesne assignments, to Beaunit Mills, Incorporated, a corporation of New York

Filed Oct. 30, 1958, Ser. No. 770,761

3 Claims. (Cl. 28-82)

This invention relates to novel and useful crimpable rayon fibers and a process for their production.

The production of crimpable filaments by extruding two or more viscoses having different shrinkage potentials through the same spinneret hole is known. While these multicomponent filaments are superior in certain respects to single component filaments, i.e. in ease of crimping and crimp retention, further improvement in the degree of crimping and crimp reversibility on wetting and drying, particularly in high denier per filament yarns, is desirable.

It is an object of this invention to provide a new and useful crimpable viscose rayon fiber.

Another object is to provide a crimpable fiber which crimps to a high degree in water, which has high bulk and improved crimp reversibility.

A further object is to provide a process for producing these fibers.

These and other objects will become apparent in the course of the following specification and claims.

In accordance with the present invention an integral rayon fiber is provided having a transverse cross section consisting of two longitudinal ribbon-like components, disposed side-by-side, a first component having a heavy, preferably at least 80% skin and a second component having an elongated narrow shape and a substantially thinner skin than the first component, one component of the fiber being wrinkled. Preferably the second component has at least 20% less skin than the first component i.e., not over 64% of the cross-sectional area.

The process comprises preparing two viscoses, A and B, adding to viscose A a small amount of coagulation modifier, extruding the two streams of viscoses simultaneously in side-by-side relationship through narrow, elongated spinneret openings into a coagulating and regenerating bath containing from about 6.5 to about 10% sulfuric acid, from about 12 to about 23% sodium sulfate, and at least about 3% zinc sulfate, viscose A having a salt index of at least about 5, viscose B having a salt index of at least about 2, the long axis of the spinneret openings being at least about 8 to 10 times the length of the short axis, and thereafter stretching the yarn. Preferably, the salt index of viscose A is at least about 3 units higher than that of viscose B.

FIGURE 1 is an exploded view of a device useful in the extrusion of the yarn of the present invention.

FIGURE 2 is a rear view of the equalizer and separator section of the device illustrated in FIGURE 1.

FIGURE 3 is an illustration of the yarn cross section produced as described in Example I.

Referring particularly to the figures the yarn produced is extruded through the orifices of the spinneret plate 2, the said plate being positioned against the equalizer and separator section 3 by means of internally threaded spinneret adapter 4, flange 5 of the spinneret plate being held against the front face of the equalizer and separator section by the face 6 of the said spinneret adapter. Concentric cylindrical separator rings 7 extend through the equalizer and separator section, the said rings being supported by the pressure equalizer plate 8 (shown in FIGURE 2) which holds them in fixed relation to the cir-

2

cumference of the said equalizer and separator section. The concentric cylindrical separator rings are beveled to a sharp edge which extends beyond the engaging threads of the equalizer and separator section to such an extent that when the spinneret plate 2 is positioned as previously described the sharp edges of the separator rings are immediately adjacent to the back face of spinneret plate 2 and so arranged that each edge bisects each orifice in a particular ring of the said orifices. Pressure equalizer plate 8 (FIGURE 2) contains concentrically arranged holes 9 fitting into spaces between the concentric separator rings previously described and act to control the pressure of, and prevent pressure surges in, viscose delivered to the spinneret plate. Pressure equalizer plate 8 fits by threaded means onto a concentric conduit 10 which contains openings 11 through which various viscoses may be pressure fed to the system.

The spinneret openings are narrow, elongated slits, preferably rectangular in shape although the openings may be rounded at the ends if desired. The long axes of the spinneret openings are at least about 8 to 10 times the length of the short axes and preferably about 16 times the length of the short axes. It is preferable that the long axis of the spinneret opening be situated radially with respect to the circular spinneret face since this greatly facilitates the extrusion of two viscoses simultaneously through the opening.

The following example is cited to illustrate the invention. It is not intended to limit it in any manner.

Example I

Two viscoses, A and B are prepared in the conventional manner. Viscose A containing 5.0% recoverable cellulose and 6.11% alkali, calculated as sodium hydroxide, is prepared from cotton linters pulp using 40% carbon disulfide based on the air dry weight of the pulp. Sufficient sodium N-methylcyclohexyldithiocarbamate is added during the mixing operation to give a concentration of 0.61% by weight. The viscose is filtered, deaerated, ripened to a viscosity of 39 poises and a salt index of 14.4. Viscose B containing 8.60% recoverable cellulose and 5.28% alkali is prepared using 30% carbon disulfide and is filtered, deaerated, and ripened to a viscosity of 46 poises and a salt index of 3.0. Viscosities A and B are then supplied to the spinneret, which has rectangular shaped openings, by means of separate gear pumps, viscose A being supplied at a rate of 48.4 g.p.m. and viscose B at 28.4 g.p.m. so that substantially equivalent amounts of recoverable cellulose are supplied by each pump. The viscoses are extruded through a spinneret of $\frac{3}{4}$ inch diameter having 50 openings of 0.002 inch width and 0.036 inch length equidistantly spaced in a ring whose diameter is $\frac{3}{8}$ inch. The long axes of the spinneret openings are disposed radially with respect to the spinneret face. The two viscoses are extruded through each of the spinneret holes in side-by-side relationship by means of the separator rings and pressure equalizer assembly previously described.

The viscoses are extruded into a coagulating and regenerating bath containing 8.0% sulfuric acid, 17.5% sodium sulfate, 9.5% zinc sulfate and maintained at a temperature of 60° C. The filaments are led for a distance of 20 inches through the bath, then over a Y convergence guide and then for a further distance of 80 inches, the yarn being confined in the bath by means of a series of roller guides.

The yarn is then led upwardly from the coagulating bath to a first power-driven feed wheel, then to a second power-driven feed wheel rotating at the same speed

as the first but having a sufficiently larger diameter to stretch the yarn 50%. A hot aqueous solution containing 2.0% sulfuric acid, 3.9% sodium sulfate and 2.1% zinc sulfate at a temperature of 95° C. is jetted onto each of the feed wheels at the top. By means of a snubber roller in combination with each feed wheel, the yarn is given a sufficient number of passes around the feed wheels to give the yarn a travel of 120 inches in this area. The yarn is led from the second feed wheel which has a peripheral speed of 50 y.p.m. downwardly to a centrifugal spinning bucket where it is wound into a cake in the conventional manner. The yarn is purified and dried in the conventional manner. The yarn denier is 1,000.

The yarn filaments are examined by cutting thin transverse cross sections in the conventional manner, dyeing these cross sections and examining them under high magnification. Cross sections are dyed following the method described by Morehead and Sisson, Textile Research Journal, 15, 444-5 (1945) except that pontamine yellow dye is substituted for calcimine yellow dye. Examination of the dyed cross section shows that one end has a heavy skin while the remainder, as shown in FIGURE 3, is narrow and elongated and has a much thinner skin. When the yarn is placed in water at 90-100° C. in a relaxed state followed by drying in a relaxed state, it is found that the yarn has an excellent spiral type of crimp. Retention of the crimp on repeated wetting and drying is found to be superior to that of two-component yarns made outside the scope of the present invention. Further examination of the yarn filaments at high magnification shows that the filaments are wrinkled or wavy on one component while the other component is substantially straight. In addition, the yarn is more bulky than other yarns having the same crimp.

The essential factor in producing the fibers of this invention is the extrusion of two streams of viscoses, one containing a coagulation modifier and the other containing no modifier, in side-by-side relationship through elongated spinneret openings to produce filaments having narrow, elongated cross sections.

The modified viscose must be spun at a salt index of at least about 5 and preferably the index is at least about 10. The unmodified viscose must be spun at an index of at least about 2 and is preferably spun at an index in the range of about 2 to about 5 although high indices may be employed in some cases. If higher indices are employed with the unmodified viscose, then the amount of modifier which is allowed to accumulate in the spinning bath due to the modifier being leached from the spinning filaments must be kept at a very low level in order to obtain the desired filament cross section.

The composition of the viscoses used in the process of this invention is not critical. Viscoscs produced with from about 27 to about 43% carbon disulfide based on the dry weight of the pulp are satisfactory. Preferably the modified viscose is produced with at least about 35% carbon disulfide. The viscose may contain from about 5.5 to about 9.5% recoverable cellulose and from about 4 to about 8% alkali.

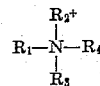
Coagulating and regenerating baths suitable for use in the present invention contain from about 6.5 to about 10% sulfuric acid, from about 12 to about 23% sodium sulfate, and at least about 3% zinc sulfate in addition to the coagulation modifier. Other metal salts which may supplement the action of the zinc sulfate may be added if desired. The acidity of the bath should be regulated to as low a level as is commensurate with satisfactory spinning.

Addition of a coagulation modifier to the viscose is necessary in order to produce the desired filament structure.

A group of preferred coagulation modifiers which are

suitable for use in the process of this invention are as follows:

(A) Quaternary ammonium compounds of the formula



X⁻, wherein the R's are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms and the fourth of the said groups containing no more than one phenyl radical, and where X⁻ is an anion having substantially no surface activity. The use of these compounds is disclosed in United States Patent 2,536,014. Suitable compounds in this group which may be mentioned are benzyltrimethylammonium hydroxide, tetraethylammonium hydroxide, tetramethylammonium chloride, phenyltrimethylammonium hydroxide, tetraethanolammonium hydroxide, tetraethylammonium bromide, tetramethylammonium iodide, tetrapropylammonium hydroxide, tetrabutylammonium chloride, tributylpropylammonium hydroxide, tri(beta-hydroxyethyl)methylammonium hydroxide, tributyl(beta-hydroxyethyl)ammonium iodide, etc. The preferred agents of this class are those in which all four organic groups attached to the nitrogen atom are hydrocarbon groups or hydroxyl-substituted hydrocarbon groups and in which the radical X is hydroxyl or halogen of atomic weight above 19, i.e., chlorine, bromine or iodine. The most useful modifiers of this group are the quaternary ammonium hydroxides having a total of not more than ten carbon atoms in the molecule and in which all organic groups are hydrocarbon or hydroxyl-substituted hydrocarbon.

(B) Aliphatic monoamines having at least four carbon atoms but containing no radical of more than six carbon atoms. The use of these compounds is disclosed in United States Patent 2,535,044. Suitable compounds in this group which may be mentioned are triethanolamine, triethylamine, diethanolamine, butylmonoethanolamine, diethylaminoethanol, n-amylamine, diethylamine, dipropylamine, n-butylamine, ethyldiethanol amine, dipropanolamine, propylpropanolamine, hexanolamine, amyldiethanolamine, butylmethylethanolamine, propylethanolamine, cyclohexylethanolamine, N-methylcyclohexylamine, hexamethyleneimine, piperidine, hexyldiethanolamine, etc. The preferred modifiers of this group are those in which the amino nitrogen is attached to hydrocarbon groups, preferably alkyl groups, and/or to hydroxyalkyl groups.

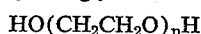
(C) Aliphatic diamines containing two amino nitrogen atoms separated only by carbon atoms and containing a total of at least three carbon atoms, said diamines having the amino groups attached to aliphatic carbon atoms, any monovalent substituent on the amino nitrogens being alkyl groups of 1 to 6 carbon atoms. The use of these compounds is disclosed in British Patent 762,772. Among the aliphatic diamines may be mentioned the following: hexamethylenediamine, tetramethylenediamine, N-methyltrimethylenediamine, N,N'-dimethylethylenediamine, N,N'-diisobutylhexamethylenediamine, N,N'-dimethyltrimethylenediamine, 4,4-dimethylhexamethylenediamine, N,N'-diethyl-1,4-cyclohexanediamine, 3-ethoxyethoxyhexamethylenediamine, pentamethylenediamine, octamethylenediamine, N-cyclohexyltetramethylenediamine, N,N'-diallylhexamethylenediamine, N-methylnonamethylenediamine, N-hexyltrimethylenediamine, N,N-dimethylpiperazine, N-butylhexamethylenediamine, etc. The preferred agents of this class are the wholly aliphatic, including cycloaliphatic, diamines which contain only carbon and hydrogen besides the two amino nitrogens and which have a total number of carbon atoms between 4 and 14, inclusive, in addition to fulfilling the other requirements stated above. Still more preferred are the polymethylenediamines of 4 to 14 total carbon atoms having from 4 to 8 methylene groups between the amino groups, and their N-alkyl substituted

derivatives where the N-alkyl groups have from 1 to 4 carbon atoms inclusive.

(D) The salts of N-substituted dithiocarbamic acids. The use of these compounds is disclosed in United States Patent 2,696,423. Among the salts of N-substituted dithiocarbamic acids may be mentioned, sodium amyl dithiocarbamate, sodium butyl monoethanol dithiocarbamate, sodium hexamethylene bis(dithiocarbamate), potassium pentamethylene dithiocarbamate, sodium methyl dithiocarbamate, sodium benzyl dithiocarbamate, sodium ethylene bis(dithiocarbamate), sodium 1,3-cyclohexane bis(dithiocarbamate), sodium dibutyl dithiocarbamate, sodium dimethyl dithiocarbamate, sodium dioctyl dithiocarbamate, sodium lauryl dithiocarbamate, sodium cyclohexyldithiocarbamate, lithium cyclohexyl dithiocarbamate, sodium N-methylcyclohexyldithiocarbamate, the sodium dithiocarbamates of a mixture of 10% hexadecylamine, 10% octadecylamine, 25% octadecenylamine and 45% octadecadienylamine, sodium hexamethylene bis(methyl dithiocarbamate), sodium ethylene bis(methyl dithiocarbamate), sodium 1,4-cyclohexane bis(ethyl dithiocarbamate), sodium xylene bis(dithiocarbamate), etc. The preferred modifiers of this class are the alkali metal salts of mono- or di-N-substituted dithiocarbamic acids containing no more than 10 carbon atoms in any radical and in which the nitrogen is attached to aliphatic carbon.

(E) The ethers of the formula $\text{RO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}'$, where R is alkyl or aryl, n is an integer from 1 to 4 inclusive; and R' is hydrogen, alkyl or aryl. The use of these compounds as coagulation modifiers is disclosed in British Patent 741,728. Among the ethers may be mentioned phenoxyethanol, ethoxyethanol, butoxyethanol, methoxyethoxyethanol, butoxyethoxyethanol, phenoxyethoxyethanol, ethoxyethoxyethoxyethanol, butoxyethoxyethoxyethanol, phenoxyethoxyethoxyethoxyethanol, 1-ethenyl-2-methoxyethylene, ethylene glycol diethyl ether, triethylene glycol diethyl ether, tetramethylene glycol diethyl ether, triethylene glycol dimethyl ether, diethylene glycol diethyl ether, etc. With this class of coagulation modifiers, it has been found that those compounds which, in addition to being soluble in viscose, are difficultly soluble in the coagulating bath, i.e., to the extent of less than 0.5%, give the best results.

(F) The polyethylene glycols of formula



where n is an integer greater than 3. The use of these compounds is disclosed in Italian Patent 561,552. The polyethylene glycols of formula $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ (ethylene oxide polymers) include all such compounds where n is at least equal to 4, i.e., polymers which have a molecular weight of at least 200, and which in addition have the required solubility in viscose. Such compounds are available commercially in various molecular weight ranges, such as 600, 1500 or 2500. For use as coagulation modifiers, the polyethylene glycols having molecular weights between about 300 and about 1000 are preferred.

Other coagulation modifiers, as are known in the art, may also be employed in place of the listed compounds. Various suitable ones are described in United States Patents 2,777,775; 2,792,278; 2,792,279; 2,792,280 and 2,792,281; British Patents 723,435; 730,541; 748,147 and 765,905, and French Patents 1,102,898 and 1,111,580.

The yarn should be stretched at least about 40% while passing through the bath. Where a hot secondary bath is used, the stretch may be concentrated in this bath or it may be divided between the two baths as desired. If a hot secondary bath is not employed, then all of the stretch is imposed on the yarn while passing through the

coagulating and regenerating bath by means of tension-type roller guides.

Preferably the ratio of the yarn draw-off speed to the linear speed at which the viscose is extruded is at least 1.0. This is particularly true where the denier per filament is low (below 8) since under these conditions the desired elongated shape of the filament cross section may not be realized if the ratio is too low. Likewise, the ratio should be at least 1.0 if the ratio of length to width of the spinneret opening is below about 8.

After the yarn leaves the bath, it is wound into a cake in a centrifugal spinning bucket or wound on a bobbin and thereafter purified and dried in the conventional manner.

After purification, the yarn is preferably given additional stretch after thorough wetting and is then dried in the stretched condition. The stretching is conveniently applied by passing the yarn through a slashing machine of the type used in the production of tire cord yarn. If the customary aqueous finish is applied to the yarn, the yarn is wetted with this before stretching.

The yarn crimps readily when allowed to relax in hot water followed by drying in a relaxed state. Instead of water, various aqueous solutions as are well known in the art may be used in the crimping operation.

The fibers of this invention may be used wherever rayon fibers are customarily employed, however, they are particularly suitable for the production of tufted carpets and cut pile fabrics.

Many modifications of the invention described herein will be apparent to those skilled in the art from a reading of the above without a departure from the inventive concept.

What is claimed is:

1. An integral regenerated cellulose rayon fiber having a cross-sectional width at least 8 times the general thickness, said fiber consisting essentially of two longitudinal ribbon-like components disposed side-by-side, one of said components having a thick skin which constitutes at least 80% of the cross-sectional area, the other of said components having a thinner skin which constitutes not over 64% of the cross-sectional area, said components having different shrinkage potentials, one of said components being wrinkled.

2. A crimpable spun yarn composed of fibers as defined in claim 1, said yarn having the capacity to spontaneously assume a spiral type of crimp when placed in water at 90–100° C. in a relaxed state followed by drying in a relaxed state.

3. An integral regenerated cellulose rayon fiber as defined in claim 1 wherein said longitudinal ribbon-like components contain substantially equal amounts of regenerated cellulose.

References Cited in the file of this patent

UNITED STATES PATENTS

1,944,378	Thenoz	Jan. 23, 1934
2,297,746	Charch	Oct. 6, 1942
2,310,785	Hermann	Feb. 9, 1943
2,428,046	Sisson et al.	Sept. 30, 1947
2,439,814	Sisson	Apr. 20, 1948
2,535,044	Cox	Dec. 26, 1950
2,572,936	Kulp	Oct. 30, 1951
2,674,025	Ladisch	Apr. 6, 1954
2,815,532	Braunlich	Dec. 10, 1957

FOREIGN PATENTS

514,638	Great Britain	Nov. 14, 1939
176,323	Switzerland	July 1, 1935