

1

2,852,333

VISCOSE SPINNING PROCESS

Norman Louis Cox, Claymont, and William Dickson Nicoll, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application May 21, 1954
Serial No. 431,576

4 Claims. (Cl. 18—54)

This invention relates to new, crimped, wool-like regenerated cellulose fibers of high tenacity and to a new process for producing these fibers.

There has recently been described, in U. S. Patent No. 2,515,834 to William D. Nicoll, a permanently crimped regenerated cellulose fiber, referred to herein as "Fiber E," which has already achieved an outstanding commercial success. This fiber is characterized by the unique property that the crimp, after being removed through stretching, combing or other mechanical means, is restored to the fiber simply by suspending it in water, or other aqueous swelling liquid, in the absence of tension. The crimp regain is practically instantaneous, whether the fiber be in the form of staple or of continuous filaments. However, these fibers are not completely satisfactory for some textile uses. The strength of these fibers is not high enough for some purposes and, because of the crenulated cross-section of the fibers, they are also less satisfactory with respect to resistance to soiling than would be the case with smooth surfaced filaments.

Accordingly, it is an object of this invention to provide an improved type of crimped fiber which has high strength and a thick substantially uniform skin with a smooth surface which imparts enhanced properties for textile uses. Another object is to provide a suitable process for preparing such a product. Other objects will become apparent from the following description and claims:

It has now been found that, by operating under a rigorously selective and narrow set of conditions and by using a viscose-soluble coagulation modifier of the type more fully described later, it is possible to produce a basically new type of crimped regenerated cellulose fiber of improved properties. This new fiber also possesses the outstanding advantage of having a permanent, restorable crimp. In addition, it is characterized by a high tenacity, generally in the neighborhood of 1 g. per denier higher than that possessed by Fiber E. This is, of course, a considerable technical advantage in practically all applications, since one of the persistently sought objects in viscose rayon manufacture is the production of yarn having increased tenacity without sacrifice in other valuable properties. Moreover, the new filaments of this invention, in contrast with other crimped filaments, have a smooth, substantially non-crenulated surface and a lower secondary swelling (water take-up by dried yarns). These properties usually result in more resistance to fibrillating, laundering, soiling and abrasion than crenulated yarns. The filaments are further characterized by an unusually high ratio of at least 1:1 of skin to core or at least 50% skin when measured radially, i. e., the ratio of lengths along a representative diameter of this filament. This compares to less than 40% for Fiber E.

The filaments of this invention are produced by a process which comprises the steps of extruding into a sulfuric acid-sodium sulfate-zinc sulfate coagulating and regenerating bath a highly xanthated, substantially unripened viscose containing dissolved therein from about 0.1

2

to about 10 millimoles per 100 g. of a viscose-soluble coagulation modifier which lowers the gel swelling factor by at least 8% and decreases the rate of neutralization of the filament by at least 50% as compared with the corresponding values for a similar but unmodified viscose spinning system, stretching the coagulated filament in a secondary, non-alkaline aqueous bath and relaxing the substantially completely regenerated filament, in the complete absence of tension, in an aqueous swelling bath, said steps being carried out with observance of the following critical conditions:

(a) The viscose has a cellulose content between 5% and 7%.

(b) The viscose has an alkali content (calculated as NaOH) between 5% and 7%.

(c) The coagulating and regenerating bath has a sulfuric acid content between 6% and 10% but not above the acidity which produces the minimum gel swelling factor.

(d) The coagulating and regenerating bath has a sodium sulfate content between 14% and 21%.

(e) The coagulating and regenerating bath has a zinc sulfate content between 6% and 15%.

(f) The temperature of the coagulating and regenerating bath is between 40 and 65° C.

(g) The filament travels between 15 and 150 inches in the coagulating and regenerating bath.

(h) The stretch, as measured in the secondary bath, is between 70% and 160%.

(i) The final tension on the filament is between 0.5 and 1.0 g./denier.

(j) The temperature of the secondary stretching bath is between 50 and 100° C.

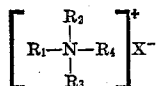
The process defined above requires, as the starting material, a highly xanthated viscose. In order to have the required amount of xanthate groups, it is necessary first that the viscose be prepared with a higher than normal quantity of carbon disulfide. It has been found that the minimum quantity of carbon disulfide required for good results is about 35%, based on the weight of the bone-dry cellulose. The maximum amount of carbon disulfide is limited only by practical considerations such as reaction time, and it can be as high as 65% or even higher. Best results are in general obtained when the viscose is prepared between 45 and 60% of carbon disulfide. It is further necessary that the viscose be spun as green (unripened) as possible. The degree of ripening (i. e., of loss of xanthate groups by decomposition) is expressed by the salt index of the viscose, which decreases as the degree of ripening increases. To achieve the full benefits of this invention, the ripening time should be cut to the minimum practicable. This is particularly true of viscoses prepared with the minimum amount of carbon disulfide (about 35%) but it applies also to viscoses prepared with a high carbon disulfide concentration, even though such viscoses retain a relatively high ratio of xanthate groups after a longer ripening time. Since the salt index of the viscose depends in part on the amount of carbon disulfide, it is not possible to give specific limits. However, it can be said in general that the salt index should not be lower than 7 with viscoses prepared with the minimum amount (about 35%) of carbon disulfide. Further, it can be said in general that the viscose should have as high a salt index as practicable. In fact, this is another advantage of the invention since the time normally required for ripening is decreased or eliminated. The salt index referred to in this discussion is the sodium chloride index, determined as specified in Reinthaler-Rowe, "Artificial Silk," 1928, page 69.

It is known that, when viscose is spun into a sulfuric acid-sodium sulfate-zinc sulfate coagulating bath in the presence of small amounts of organic compounds of cer-

tain specific classes, which compounds will be referred to hereinafter as "coagulation modifiers" for the sake of brevity, new regenerated cellulose yarns having remarkable properties are obtained. This discovery has recently been published and claimed in U. S. Patents 2,535,044, 2,535,045 and 2,536,014, all to N. L. Cox, and other aspects of it are disclosed and claimed in application serial No. 228,975, filed May 29, 1951, now Patent No. 2,696,423, by M. A. Dietrich, now U. S. P. 2,696,423; British Patent 741,728 and British Patent 762,772. In these patents and applications it is shown that the various classes of organic compounds which have been found effective as coagulation modifiers all have two characteristics in common: they lower the gel swelling factor of the regenerated cellulose filaments and they lower the rate of neutralization of the viscose filament in the coagulating and regenerating bath. Both of these characteristics are associated with the extraordinary improvements in yarn and cord properties which result from the use of these coagulation modifiers.

The coagulation modifiers which have been found suitable for use in the process of this invention include the following. In each case, it is understood that these agents are soluble in the viscose at least to the extent specified below:

A. The quaternary ammonium compounds of the formula



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 as coagulation modifiers is disclosed and claimed in U. S. Patent No. 2,536,014.

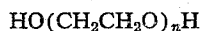
B. The aliphatic monoamines having at least four carbon atoms but containing no radical of more than six carbon atoms. The use of these compounds as coagulation modifiers is disclosed and claimed in U. S. Patent No. 2,535,044.

C. The 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 as coagulation modifiers is disclosed in British Patent 762,772.

D. The salts of N-substituted dithiocarbamic acids. The use of these compounds as coagulation modifiers is disclosed and claimed in application Serial No. 228,975, filed by M. A. Dietrich on May 29, 1951, now U. S. P. 2,696,423.

E. The ethers of the formula $RO-(CH_2CH_2O)_nR'$, where R is alkyl or aryl; n is an integer from 1 to 4 inclusive and R' is hydrogen, alkyl or aryl, said ethers being soluble in the coagulating bath to the extent of not more than 0.5%. The use of these compounds as coagulation modifiers is disclosed in British Patent 741,728.

F. The polyethylene glycols of formula



where n is at least equal to 4. These compounds have also been found useful as coagulation modifiers and they are disclosed for that use in application Serial No. 228,975, filed by M. A. Dietrich on May 29, 1951, now U. S. P. 2,696,423.

Agents of the various chemical classes listed must also fulfill the requirement of being soluble in the viscose, since it has been found that, if solubility is incomplete, or, in other words, if an emulsion or dispersion of the

agent in the viscose is present, the desired results are not obtained. For good results, it has been found that the coagulation modifier should be soluble in 6% aqueous sodium hydroxide to the extent of at least 0.05%. Agents having a solubility above this limit are sufficiently soluble in viscose to give the desired effects.

As already stated, the acidity of the bath must not exceed that value which produces the minimum gel swelling factor. Gel swelling factors are determined as described in U. S. Patent No. 2,515,834. Likewise, the rate of neutralization is expressed, as in U. S. Patent No. 2,535,044, in terms of the "D" value, which is the distance in inches from the spinneret to the point where the color of a suitable indicator added to the viscose disappears in the traveling filament.

With respect to the coagulating and regenerating bath, the stated ranges of concentration of the three essential components, viz., sulfuric acid, sodium sulfate, and zinc sulfate, must be observed in order to realize the benefits of this invention, and likewise the temperature of the bath must be within the stated limits. Provided these restrictions are observed, it is permissible to have present, if desired, other bath components well known in the viscose spinning art, such as glucose or similar organic substances. The length of travel of the filament in the bath is in general much shorter than normal, and the filament receives but little stretch, or often no stretch at all, during its passage through the bath.

The necessary stretch on the filament is applied after it leaves the coagulating bath. This is done by passing the filament through a secondary aqueous bath (referred to in the trade as "hot-dip") maintained at a temperature above 50° C., and preferably in the neighborhood of, or above 90° C. In the process of the invention, the secondary bath is non-alkaline and consists generally of water or of dilute (1-3%) sulfuric acid, but it may also have the same composition as the coagulating bath but diluted, for example, one fourth the concentration, and in any case it is usually weakly acidic because of the acid carried over from the coagulating bath by the filament. During the passage of the filament through the secondary bath, a substantial degree of stretch is imposed on it by suitable mechanical devices, in the range of 70% to 160% of the unstretched length of the filament. The final tension on the filament, as measured at the end of the secondary bath, should be in the range of 0.5 to 1.0 g./denier.

The gel yarn is normally collected on a bobbin and washed free of acid and salt on the bobbin before the relaxing step. However, the spinning can equally well be carried out by the bucket process. Optimum crimpability is obtained by drying the yarn under tension before the relaxing step, but this is optional and it is often preferred to pass the filament directly from the secondary bath, with or without passage through a washing bath, into the relaxing bath, either in the form of continuous filaments or of staple fibers.

The relaxing bath may be composed of any liquid which is capable of moderately swelling the cellulose filaments. It is preferable to avoid baths which have a strong swelling action, because such baths, although they produce good crimp, tend to decrease the tenacity of the resulting filaments. In general, it may be said that the relaxing bath should swell the filament by an amount not exceeding about 100% (i. e., the diameter of the wet filament does not increase by more than about 100% over that of the dry filament). Since the filaments will be substantially regenerated by the time they are subjected to relaxation in the relaxing bath, the latter will have substantially no regenerating action on the filaments. The relaxing bath preferably comprises water and it may be slightly acidic, neutral or slightly alkaline. The relaxing bath may contain an acid or a salt such as calcium chloride, sodium thiocyanate, calcium thiocyanate or the like. Such salts will often impart a particularly desired swelling action to the filaments whereby crimping takes place

in a particularly desirable manner. The relaxing bath may also contain agents such as sodium carbonate and caustic soda, which also have a desirable swelling action on the filaments. For example, it is possible to use as the relaxing bath 0.5–2% aqueous solutions of sodium hydroxide. The temperature of the relaxing bath may vary rather widely, as this is not very critical. However, it is normally between 0° C. and 120° C. When using water alone, the bath temperature is preferably above 50° C., for example, 75–100° C. Relaxing baths consisting of aqueous alkaline solutions such as aqueous sodium hydroxide are preferably used at temperatures between 20 and 50° C. The relaxing bath may comprise or consist of organic liquids such as glycerol if the latter is used at a temperature of the order of 120° C., at which temperature glycerol swells regenerated cellulose filaments.

Whatever the composition and temperature of the relaxing bath are, the filaments must be allowed to rest in the relaxing bath free of all tension and must be free to shrink to the maximum extent. One of the best methods of securing complete relaxation is to immerse the skeins or staple in the relaxing bath, making sure that there is ample room for the fibers to crimp freely and shrink. If the filaments are not free from all tension, as for example, when they are allowed to relax only partially in a wash and bleach machine by hanging skeins on a rod under the weight of a large amount of liquid, the results are found to be unsatisfactory. The time of immersion of the filaments in the relaxing bath is not critical. Under the proper conditions of relaxation, the crimp will be formed in the fibers in the relaxing bath practically instantaneously.

The filament may be washed acid free, desulfured and/or bleached prior to the time it is immersed in the relaxing bath, or it may be relaxed while in the acid state and then washed, desulfured and/or bleached after crimping has been accomplished. If the filament is crimped before the acid is removed, hot water is the preferred relaxing agent, as alkaline solutions give less satisfactory results. However, if the acid is removed before crimping, either water or a caustic relaxing bath can be used.

The following examples illustrate the invention but are not to be construed as limitative:

Example I

Viscose containing 0.1% by weight (1.0 millimole per 100 g.) of cyclohexylamine was prepared in the following manner to give a final product containing 6% cellulose and 6% total sodium hydroxide. Cotton linters cellulose (unaged, so as to get the desired viscose viscosity of 40–60 poises) was xanthated for 2½ hours using 62% carbon disulfide, based on the recoverable bone-dry cellulose. The xanthate crumbs were dissolved in aqueous sodium hydroxide containing the cyclohexylamine. After mixing for 1½ hours at 0° C., the freshly prepared viscose was filtered cold, deaerated and kept at 0° C. until spun. In this and the following examples, the caustic content refers to the total alkalinity expressed as sodium hydroxide. It includes the coagulation modifier, when the latter is basic, the free sodium hydroxide, and that combined in the form of sodium carbonate, sodium trithiocarbonate, and sodium cellulose xanthate.

The viscose was spun in the unripened state (salt index about 22, high xanthate sulfur content) into a 275 denier-120 filament yarn by extruding through a spinneret having holes of 0.0025 inch diameter into a primary coagulating and regenerating bath containing 6% sulfuric acid, 17% sodium sulfate and 10% zinc sulfate at 50° C. The spinning speed was 28 yards per minute and the yarn was given a bath travel of 25 inches by using a roller guide. The apparatus and general procedure used to lead the viscose into the bath and to collect the formed thread were essentially the same as those used commercially in the so-called bobbin or spool process. After leaving

the primary bath, the filaments were carried through a water bath at 95–100° C. and wound up at such a speed as to give a 145% stretch beyond the feed wheel and a total tension on the yarn of 0.76 g./den. The resulting regenerated gel yarn was washed free of acid and salt on the bobbin. A wet skein of the yarn was then immersed, completely free from tension, in a hot water bath, whereupon it crimped instantaneously. The crimp was permanent, i. e., when removed by mechanical means, it was immediately restored by immersing the yarn, free from tension, in hot water or in dilute aqueous sodium hydroxide. This yarn, prior to relaxation, had a dry tenacity of 4.30 g./den., a wet tenacity of 2.58 g./den., a dry elongation of 5.9% and a wet elongation of 15.5%. Experience has shown that, as a rule, the yarn after relaxation does not lose more than about 25% of its dry tenacity prior to relaxation.

Example II

A viscose containing 0.1% by weight (1.0 millimole per 100 g.) of cyclohexylamine was prepared as in Example I, except that it contained 5% cellulose and 6% total sodium hydroxide and that the amount of carbon disulfide used was 50%, based on the bone-dry cellulose. This viscose was spun in the unripened state (salt index about 16.5), using the procedure and conditions of Example I except that the coagulating and regenerating bath contained 7.7% sulfuric acid rather than 6.0%, the stretch in the hot-dip bath was 131% and the final tension on the yarn 0.59 g./den. The yarn was washed on the bobbin, dried on the bobbin and the resulting skein immersed free from tension in hot water. A yarn having a good permanent crimp resulted. This yarn, after relaxation, had a dry tenacity of 3.20 g./den., a wet tenacity of 2.19 g./den., a dry elongation of 12.2% and a wet elongation of 13.9%.

Example III

A viscose containing 0.1% by weight of cyclohexylamine was prepared as in Example I, except that it contained 5% cellulose and 6% total sodium hydroxide and that the amount of carbon disulfide used was 60%, based on the bone-dry cellulose. The viscose was spun in the unripened state (salt index about 23.5), using the procedure and conditions of Example I except that the coagulating bath contained 8.8% sulfuric acid, the length of travel of the filament in the coagulating bath was 150 inches, the stretch in the hot-dip bath was 108% and the tension 0.97 g./den. The yarn was washed and dried on the bobbin before relaxation, then immersed free from tension in hot water. The resulting permanently crimped yarn had, after relaxation, a dry tenacity of 3.23 g./den., a wet tenacity of 2.23 g./den., a dry elongation of 19.8% and a wet elongation of 20.7%.

Example IV

A viscose was prepared of the same composition as in Example III, except that it contained 0.06% by weight (0.61 millimole per 100 g.) of cyclohexylamine. This viscose was spun in the unripened state (salt index about 23), using the procedure and conditions of Example I except that the spinneret was such as to give an 1100 denier-480 filament yarn, the coagulating bath contained 6.5% sulfuric acid, the length of travel of the filament in the coagulating bath was 30 inches, the stretch in the secondary bath was 155% and the tension 0.97 g./den. The filament was washed and dried on the bobbin, then relaxed free from tension in hot water. After relaxation, the permanently crimped yarn had a dry tenacity of 3.12 g./den., a wet tenacity of 2.72 g./den., a dry elongation of 19.4% and a wet elongation of 30.2%.

Example V

A viscose containing 0.3% by weight of polyethylene glycol of molecular weight about 300 (6.8 millimoles

per 100 g., the mole being understood as the recurring polymer unit) was prepared as described in Example I, but from cotton liners alkali cellulose which had been given the normal aging for a viscose viscosity of 40-60 poises. The composition of the viscose was 7% cellulose and 6% total sodium hydroxide and it was prepared using 35% carbon disulfid, based on the bone-dry cellulose. The viscose was spun in the unripened state (salt index about 10), in a coagulating and regenerating bath containing 6% sulfuric acid, 14% sodium sulfate and 13% zinc sulfate, the spinning conditions being those of Example I except that the stretch in the hot-dip bath was 160% and the spinning tension was 0.6 g./den. The yarn was washed on the bobbin and relaxed in hot water without prior drying, whereby it acquired a permanent crimp. This yarn, prior to relaxation, had a dry tenacity of 4.43 g./den., a wet tenacity of 2.88 g./den., a dry elongation of 6.2% and a wet elongation of 12.0%.

Example VI

A viscose having the same composition as that of Example V, except that it contained 0.15% by weight (0.76 millimole per 100 g.) of sodium cyclohexyldithiocarbonate as the coagulation modifier, was prepared from normally aged alkali cellulose. This viscose was spun in the unripened state (salt index about 9, xanthate sulfur about 1.65%) in a bath containing 6.1% sulfuric acid, 14% sodium sulfate and 13% zinc sulfate, all spinning conditions being as in Example I except that the travel in the primary bath was 150 inches, the stretch in the secondary bath was 108% and the spinning tension was 0.86 g./den. The yarn was washed on the bobbin and immersed without drying in hot water, whereby it acquired a permanent crimp. Prior to relaxation, this yarn had a dry tenacity of 3.7 g./den., a wet tenacity of 2.5 g./den., a dry elongation of 5.4% and a wet elongation of 13.7%.

Example VII

A viscose containing 5% cellulose, 6% total alkali and 0.1% (1.0 millimole per 100 g.) of cyclohexylamine was prepared from unaged alkali cellulose, using 50% carbon disulfide based on the bone-dry cellulose. This viscose was spun in the unripened state into a bath at 50° C. containing 8% sulfuric acid, 17.5% sodium sulfate and 9.5% zinc sulfate. The spinning speed was 30 yards per minute and the length of travel of the filament in the primary bath was 50 inches. The yarn was then stretched in a secondary hot water bath, the spinning tension being 1.0 g./den., washed and dried on the bobbin, then immersed free from tension in a 1% aqueous sodium hydroxide solution, whereby it acquired a permanent crimp. After relaxation, this yarn had a dry tenacity of 3.3 g./den., a wet tenacity of 2.3 g./den., a dry elongation of 23% and a wet elongation of 27%.

In connection with the process just described in detail, it is emphasized again that the specifically enumerated process factors are all interdependent and that they must be adjusted in relation to one another to obtain the desired result, i. e., a satisfactory crimp.

It is, of course, understood that relaxing of the filaments, completely free of all tension, in an aqueous medium is absolutely essential, no matter what variations may be introduced in the other conditions. It is also essential that the viscose contain a coagulation modifier capable of lowering the gel swelling factor by at least 8% and of decreasing the rate of neutralization of the filament by at least 50%. Finally, it is essential that the viscose be spun in the unripened state, which means in practice at a minimum salt index of 7 for a 35% CS₂ viscose, and at correspondingly higher salt indices for viscoses made with higher amounts of carbon disulfide.

For each of the process factors enumerated above, the range within which the process may be successfully operated has been indicated, but it will be apparent that, if any one of the factors is set at or near the extreme lower

or upper limit of its particular range, other factors may have to be adjusted in order to obtain the best results. To illustrate, if the acid content of the coagulating bath is 6% (the lowest limit of the range) either the sodium sulfate content or the zinc sulfate content or both should be correspondingly increased above their lowest permissible values.

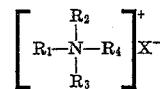
For the purpose of making this process more readily understandable, the following table will be useful to show both the operable ranges and the optimum ranges.

	Operable Range	Optimum Range
Cellulose content of viscose.....percent..	5-7	5-6
Alkali content of viscose.....do.....	5-7	5.5-6
Sulfuric acid in the bath.....do.....	6-10	6-8.5
Sodium sulfate in the bath.....do.....	14-21	14-18
Zinc sulfate in the bath.....do.....	6-15	9.5-13
Temperature of coagulating bath.....°C.....	40-65	50-60
Length of bath travel.....inches.....	15-150	15-35
Stretch in secondary bath.....percent.....	70-160	100-140
Final tension.....g./den.....	0.5-1.0	0.7-0.9
Temperature of secondary bath.....°C.....	50-100	80-100

Although no definite rules can be given for making all necessary adjustments permitting one to use conditions outside of optimum ranges but still within the operable range, it can be said, in general, that not more than three of the relationship factors should be outside of an optimum range.

With respect to the coagulation modifier, suitable agents in addition to those mentioned in the examples include the following:

A. Among the quaternary ammonium compounds of the formula



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 containing no more than one phenyl radical, and where X⁻ is an anion having substantially no surface activity, the following may be mentioned: benzyltrimethylammonium hydroxide, tetramethylammonium hydroxide, tetramethylammonium chloride, phenyltrimethylammonium hydroxide, tetraethanolammonium hydroxide, tetraethylammonium bromide, tetramethylammonium iodide, tetrapropylammonium hydroxide, tetrabutylammonium chloride, tributylpropylammonium hydroxide, tri(β-hydroxyethyl)methylammonium hydroxide, tributyl(β-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 group 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. Among the aliphatic acyclic or alicyclic primary, secondary or tertiary monoamines having at least four carbon atoms but containing no radical of more than six carbon atoms may be mentioned triethanolamine, triethylamine, diethanolamine, butylmonoethanolamine, diethylaminoethanol, n-amylamine, diethylamine, dipropylamine, n-butylamine, ethyldiethanolamine, dipropylamine, propylpropanolamine, hexanolamine, amyl-diethanolamine, butylmethylethanolamine, propylethanolamine, cyclohexylethanolamine, hexamethyleneimine, piperidine, hexyldiethanolamine, cyclohexylamine and N-methylcyclohexylamine. Preferred are those in which the amino nitrogen is attached to hydrocarbon groups, preferably alkyl groups, and/or to hydroxyalkyl groups.

C. Among the aliphatic diamines containing a total of at least three carbon atoms and having the amino groups attached to aliphatic carbon atoms, the amino groups being separated by a chain of only carbon atoms and any monovalent substituent on the amino nitrogen being alkyl group of 1 to 6 carbon atoms, may be mentioned the following: hexamethylenediamine, tetramethylenediamine, N-methyltrimethylenediamine, N,N'-dimethyltrimethylenediamine, 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. Among the salts of N-substituted dithiocarbamic acids may be mentioned sodium amyl dithiocarbamate, sodium N-methylcyclohexyl 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 dimethyldithiocarbamate, sodium dioctyl dithiocarbamate, sodium lauryl dithiocarbamate, sodium or lithium cyclohexyl dithiocarbamate, the sodium dithiocarbamates of a mixture of 10% hexadecylamine, 10% octadecylamine, 35% octadecylamine and 45% octadecadienylamine, sodium hexamethylene bis(methyl dithiocarbamate), sodium ethylene bis(methyl dithiocarbamate), sodium 1,4-cyclohexane bis(ethyl dithiocarbamate), sodium xylylene 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. Among the ethers of the formula



where R is alkyl or aryl, n equals 1, 2, 3, or 4 and R' is hydrogen, alkyl or aryl may be mentioned phenoxyethanol, ethoxyethanol, methoxyethoxyethanol, butoxyethoxyethanol, phenoxyethoxyethanol, ethoxyethoxyethoxyethanol, butoxyethoxyethoxyethanol, phenoxyethoxyethoxyethanol, butoxyethoxyethoxyethoxyethanol, phenoxyethoxyethoxyethoxyethoxyethanol, 1-ethenyloxy-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 only 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 desired results.

F. The polyethylene glycols of formula



(ethylene oxide polymers) include all such compounds where n is at least equal to 4, i. e., polymers which have a molecular weight at least in the neighborhood of 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 100 are preferred.

It will be understood that it is possible, and sometimes desirable, to use mixtures of two or more coagulation modifiers, which may belong to the same chemical class or to different ones.

For effective results, the modifiers should be used in the viscose in concentration of at least 0.1 millimole per 100 g. of viscose. In general, it is unnecessary to use more than 10 millimoles of the agent per 100 g. of viscose, a generally useful range being 0.5 to 4.0 millimoles per 100 g. of viscose. In terms of the less informative weight percent basis, there should be used between about 0.008% and 1% of the modifying agent. It will be understood that these concentrations depend to some extent on the nature and effectiveness of the coagulation modifier. For example, it is in general indicated to use a larger amount of a quaternary ammonium compound modifier than of a diamine modifier. The most effective concentration also depends to some extent on process variables such as the spinning speed, since at the high spinning speeds used in industrial practice less agent is desirable than at lower speeds, for the reason that the rate of neutralization of the filament should be retarded only to the extent compatible with complete coagulation during the short time the filament is in contact with the coagulating bath.

As has already been stated, coagulation modifiers of the types recited have the common property of lowering the gel swelling factor by at least 8% and the rate of neutralization (as measured by the increase in "D" value) by at least 50%, in comparison with the corresponding values for identical, but unmodified, viscose spinning systems. The great majority of these compounds lower the gel swelling value by over 10% and decrease the rate of neutralization by at least 75%.

The viscoses used in the process of this invention may be of a variety of types. They may be prepared from wood pulp, cotton linters or mixtures of the two, or from other types of cellulose.

The yarn produced by the process of this invention has a new and unique combination of properties. Like the yarn described in U. S. Patent No. 2,515,834, it is crimped, and its crimp has the permanence already described, i. e., upon being mechanically removed, it is substantially completely restored by suspending the filament, free from tension, in an aqueous liquid. The curly crimp in the fibers produced in accordance with this invention is durable and produces a pleasing, wool-like appearance and hand. In the case of fibers which have been cut to staple length before being permitted to relax in an aqueous relaxing bath, the crimps obtained are quite irregular, both as to their number per inch and their arrangement around the fiber axis. It is difficult, therefore, to define the degree of crimp obtained in these fibers in a quantitative manner, but it may be said in general that the number of crimps along the axis of the unstretched fiber is usually in the neighborhood of 8 to 15 crimps per inch.

The fibers of this invention are characterized by high tenacity, on the average about 1.0 g. per denier higher than the average fiber of U. S. Patent No. 2,515,834. In general, the fibers of this invention have, after relaxation, a dry tenacity higher than 3 g./den. and a wet tenacity higher than 2.2 g./den. Particularly remarkable tenacity values are obtained when the filament is spun at low speed, e. g., 25-30 yards per minute. At higher spinning speeds, e. g., 105 yards per minute, the tenacity figures are somewhat lower. The dry elongation is in general of the order of 15 to 23%, the wet elongation of the order of 18 to 28%, and the ratio of wet to dry tenacity is high, in general above 0.6:1.

Notwithstanding their crimped character, the fibers of this invention are basically entirely different from the previously described crimped fibers. The most readily apparent new features are the cross-section and the surface. Cross-sections of the filaments of this invention show no appreciable crenulation and thus have fairly regular, rather than indented, contours. As a result, the surface of the filament is smooth. The cross-section shows further that the boundary between the skin and core is diffuse, that the peripheral skin thickness is essentially uniform, and that the ratio of skin to core is very high. When measured radially along typical diameters, the skin represents at least 50% and usually more than 60% of the radial measurement, and can approach or even equal 100%, i. e., a filament which is substantially all skin. It is more convenient to make this comparison of skin to core along a representative diameter of the filament, rather than estimating relative areas, and the percentage of skin is more significant. Thus, 90% skin based on area would only be about 65% by radial measurement.

The filaments of this invention, having smooth surfaces, have more resistance to fibrillating, laundering, fatiguing and soiling action than normal crenulated viscose filaments. Moreover, they have a considerably lower secondary swelling (water take-up by dried yarns) than normal viscose yarns. The filaments of this invention have a secondary swelling less than about 80%, in general of the order of 65 to 80%.

The mechanism of the crimp formation in the filaments of this invention is not known. A possible explanation involves differential shrinkage, caused by differences in strain between skin and core, which causes the filament to buckle when it is relaxed in a swelling medium under tensionless conditions. The postulated shrinkage differential is presumed to be a result of stretching the filament while large differences exist in the state of regeneration between the inner and outer parts of the filament. This is accomplished by critical adjustment of the various process factors, e. g., adjustment of bath acidity in combination with the alkali, carbon disulfide and coagulation modifier present in the viscose. In this connection, it is believed that the low cellulose content of the viscose is particularly significant in the production of high tenacity crimped fibers since it is believed that the higher degree of gel swelling produced by the low cellulose content is of considerable importance. The net effect of these and other variables is to produce an unbalance in the coagulation process which then produces an unbalance in the tensions built up within the fine structure of the fiber.

Continuous filament yarn comprising crimped filaments of the type described above is particularly desirable for the production of woven and knit goods (e. g., fabrics, blankets, rugs, carpets, sweaters, wearing apparel, etc.) where more than average yarn strength, together with a wool-like hand, is desired. The crimped staple fibers of the present invention are very desirable for the production of a unique and superior yarn. Fabrics produced from either continuous filament or spun yarn made in accordance with this invention have a very desirable hand.

Since many different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

What is claimed is:

1. A process for the production of high tenacity, crimped regenerated cellulose filaments which comprises the steps of spinning filaments by extruding into a sulfuric acid-sodium sulfate-zinc sulfate coagulating and regenerating bath a viscose which is highly xanthated with at least 35% of carbon disulfide based on the cellulose content, is substantially unripened at a salt index of at least 7, and contains dissolved therein about 0.1 to 10 millimoles per 100 grams of viscose of a coagulation modifier which lowers the gel swelling factor by at least

8% and decreases the rate of neutralization of the filament by at least 50% as compared with corresponding values for a similar but unmodified viscose spinning system, then stretching the coagulated filaments in a non-alkaline aqueous secondary bath, and finally relaxing the substantially completely regenerated filaments in the complete absence of tension in an aqueous swelling bath, said steps being carried out with observance of the following critical conditions:

- (a) The viscose has a cellulose content between 5% and 7%,
 - (b) The viscose has an alkali content (calculated as NaOH) between 5% and 7%,
 - (c) The coagulating and regenerating bath has a sulfuric acid content between 6% and 10% but not above the acidity which produces the minimum gel swelling factor,
 - (d) The coagulating and regenerating bath has a sodium sulfate content between 14% and 21%,
 - (e) The coagulating and regenerating bath has a zinc sulfate content between 6% and 15%,
 - (f) The temperature of the coagulating and regenerating bath is between 40 and 65° C.,
 - (g) The filament travels between 15 and 150 inches in the coagulating and regenerating bath,
 - (h) The stretch, as measured in the secondary bath, is between 70% and 160%,
 - (i) The final tension on the filament is between 0.5 and 1.0 gram per denier,
 - (j) The temperature of the secondary stretching bath is between 50 and 100° C., with not more than three of said critical conditions being outside of the following optimum ranges:
- | | |
|--|------------|
| (a) Cellulose content of viscose.....percent.... | 5 to 6 |
| (b) Alkali content of viscose.....do..... | 5.5 to 6 |
| (c) Sulfuric acid in the bath.....do..... | 6 to 8.5 |
| (d) Sodium sulfate in the bath.....do..... | 14 to 18 |
| (e) Zinc sulfate in the bath.....do..... | 9.5 to 13 |
| (f) Temperature of coagulating bath...° C.... | 50 to 60 |
| (g) Length of travel in coagulating bath | |
| inches.... | 15 to 35 |
| (h) Stretch in secondary bath.....percent.... | 100 to 140 |
| (i) Final tension.....g. p. d.... | 0.7 to 0.9 |
| (j) Temperature of secondary bath...° C.... | 80 to 100 |

2. A process as defined in claim 1 wherein the highly xanthated viscose is prepared with between 45 and 60% of carbon disulfide, based on the cellulose content.

3. A process as defined in claim 1 wherein the coagulation modifier is soluble in 6% aqueous sodium hydroxide to the extent of at least 0.05%.

4. A process for producing high tenacity regenerated cellulose filaments having the property of spontaneously crimping upon being suspended free of tension in an aqueous liquid which comprises the steps of spinning filaments by extruding into a sulfuric acid-sodium sulfate-zinc sulfate coagulating and regenerating bath a viscose which is highly xanthated with at least 35% of carbon disulfide based on the cellulose content, is substantially unripened at a salt index of at least 7, and contains dissolved therein about 0.1 to 10 millimoles per 100 grams of viscose of a coagulation modifier which lowers the gel swelling factor by at least 8% and decreases the rate of neutralization of the filament by at least 50% as compared with corresponding values for a similar but unmodified viscose spinning system and thereafter stretching the coagulated filaments in a non-alkaline aqueous secondary bath, said steps being carried out with observance of the following critical conditions:

- (a) The viscose has a cellulose content between 5% and 7%,

13

(b) The viscose has an alkali content (calculated as NaOH) between 5% and 7%,

(c) The coagulating and regenerating bath has a sulfuric acid content between 6% and 10% but not above the acidity which produces the minimum gel swelling factor,

(d) The coagulating and regenerating bath has a sodium sulfate content between 14% and 21%,

(e) The coagulating and regenerating bath has a zinc sulfate content between 6% and 15%,

(f) The temperature of the coagulating and regenerating bath is between 40 and 65° C.,

(g) The filament travels between 15 and 150 inches in the coagulating and regenerating bath,

(h) The stretch, as measured in the secondary bath, is between 70% and 160%,

(i) The final tension on the filament is between 0.5 and 1.0 grams per denier,

(j) The temperature of the secondary stretching bath is between 50 and 100° C., with not more than three of said critical conditions being outside of the following optimum ranges:

14

(a) Cellulose content of viscose--percent-- 5 to 6

(b) Alkali content of viscose-----do----- 5.5 to 6

(c) Sulfuric acid in the bath-----do----- 6 to 8.5

(d) Sodium sulfate in the bath-----do----- 14 to 18

(e) Zinc sulfate in the bath-----do----- 9.5 to 13

(f) Temperature of coagulating bath--° C-- 50 to 60

(g) Length of travel in coagulating bath
inches-- 15 to 35

(h) Stretch in secondary bath----percent-- 100 to 140

(i) Final tension-----g. p. d-- 0.7 to 0.9

(j) Temperature of secondary bath--° C-- 80 to 100

References Cited in the file of this patent

UNITED STATES PATENTS

2,439,813	Kulp et al.	Apr. 20, 1948
2,439,814	Sisson	Apr. 20, 1948
2,442,331	Cresswell	June 1, 1948
2,515,834	Nicoll	July 18, 1950
2,535,044	Cox	Dec. 26, 1950
2,536,014	Cox	Dec. 26, 1950
2,593,466	MacLaurin	Apr. 22, 1952
2,620,258	McLellan	Dec. 2, 1952
2,686,104	Clark	Aug. 10, 1954
2,696,423	Dietrich	Dec. 7, 1954

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,852,333

Norman Louis Cox et al.

September 16, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 42, for "claims:" read -- claims. --; line 63, for "yans" read -- yarns --; column 2, line 45, before "between" insert --with--; line 50, after "increases" insert a period; column 3, lines 8 and 9, strike out "now Patent No. 2,696,423,"; column 10, line 6, for "100" read -- 1000 --

Signed and sealed this 25th day of November 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents