

1

2,879,170

CHEMICAL COMPOSITION AND PROCESS

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9 Claims. (Cl. 106—165)

The present invention relates to a novel and useful composition and process for the production of shaped structures of regenerated cellulose. More particularly, it relates to a composition and process for the formation of shaped structures of regenerated cellulose such as filaments, ribbons, films and the like having improved properties.

It is known that the properties, particularly the strength, of viscose yarns and cords are improved through reduction of the primary swelling of the gel fibers. The great importance of gel swelling in viscose spinning operations has attained full recognition in recent years and it has become common practice to add certain compounds to the viscose, to the coagulating and regenerating bath or both to obtain the maximum reduction in the gel swelling of the freshly regenerated filaments. A number of these coagulations modifiers are described in U. S. Patents 2,535,044, 2,535,045, 2,536,014, 2,696,423, British Patents 762,772, 741,728 and Italian Patent 561,552. It is also well known that the application of increased stretch during the spinning operation leads to yarns having higher strength. Increased stretch may be attained by increasing the number of xanthate groups present during the spinning operation so that the yarn is more plastic. This may be accomplished by the use of spinning baths which coagulate the filaments but do not regenerate the cellulose. When such baths are used however, the gel swelling of the filaments is high and cannot be reduced even by the use of the above-mentioned coagulation modifiers. It is therefore highly desirable to develop methods by which the xanthate content of the yarn during the spinning operation may be increased sufficiently to permit substantial increases in stretch while at the same time maintaining a desirably low level of gel swelling.

It is an object of this invention therefore to provide a composition and process for producing yarns and cords having improved properties. Another object is to provide a process in which the xanthate content of the filaments during the spinning operation is substantially increased while the gel swelling is maintained at a desirably low level. A further object is to provide a process in which the spinning stretch may be increased while maintaining the gel swelling at a low level. Other objects will become apparent hereinafter from the descriptions, the examples and the claims.

These objects are accomplished by the present invention which provides an improvement in the process of producing a shaped structure of regenerated cellulose by extruding viscose into an acid-zinc sulfate bath in the presence of a coagulation modifier, the improvement comprising adding at least about 0.02% soluble nickel (by weight) to the viscose prior to extrusion. By the term "acid-zinc sulfate bath" is meant a conventional coagulating bath containing acid and dissolved zinc sulfate. The term "coagulation modifier" is used to designate a chemical compound which reduces the primary

2

swelling of the gel fibers. The coagulation modifier may be dissolved in either the viscose or the acid-zinc sulfate bath or both, but it is preferred that it be present in the viscose. Among the coagulation modifiers which may be used in the practice of this invention are those which are set forth in the hereinbefore mentioned patents. The term "soluble nickel" is used to designate that nickel is added to the viscose in a soluble form (i. e. it is soluble at least to the required extent—0.02%) or is converted to a soluble form upon its addition to the viscose. In either procedure the concentration of elemental nickel in the viscose must be at least about 0.02% by weight.

The present invention also provides a composition of matter comprising viscose containing at least about 0.02% of soluble nickel; which composition is useful in carrying out the above described process.

In forming the composition of the present invention, the nickel is added to the viscose in the form of a water soluble compound such as the acetate, chloride, nitrate, sulfate or as a complex compound such as the ethylenediamine tetraacetate-nickel complex or any of the various nickel ammonium compounds. Preferably the nickel is added as the nickel-ethylenediamine tetraacetate complex since in this form the nickel may be easily added without fear of precipitation as nickel sulfide due to the presence of sulfide in the viscose. Another preferred method of addition is to add the nickel as the nickel trithiocarbonate since this also eliminates the possibility of nickel sulfide precipitation. When compounds such as the acetate, chloride, nitrate, sulfate, etc. are employed, the compound must be added to the viscose very slowly as a dilute, aqueous solution while stirring the viscose vigorously to prevent precipitation of nickel sulfide. Although the nickel is added in the form of a nickel compound, for convenience the concentrations of nickel are expressed in terms of elemental nickel.

In the following examples the gel swelling of the yarn is determined on small samples (5–10 grams) of the freshly spun yarn which is collected on a bobbin or feed wheel prior to its entry into the hot secondary bath. The sample is centrifuged at 3600 r.p.m. for five minutes, weighed, washed free of acid and salt, dried in an oven at 105° C.–110° C. and weighed again. The ratio of the first weight (i. e. the weight of the centrifuged sample) to the final weight provides the grams of gel yarn per grams of dry cellulose and is referred to as the gel swelling.

The xanthate content of the filaments is determined as follows:

Sufficient yarn to give a sample of 0.05–0.10 gram of cellulose is collected by allowing the yarn to drop freely from one of the power driven rollers used to stretch the yarn, into a pH 6.5 buffer solution at 0° C.; the buffer solution consisting of 22.5 grams per liter of monosodiumphosphate with sufficient sodium hydroxide added to adjust the pH to 6.5. The yarn samples are washed three times with the buffer solution at 0° C., once with acetone and then given a final wash with the buffer solution. The washed yarn samples are then dissolved in a 100 ml. volume of 8% sodium hydroxide solution. The weight of cellulose is determined on a measured portion of the solution by the well-known dichromate oxidation procedure. The xanthate content of the sample is then determined by measuring the absorbance of the solution at 302 mμ using a Beckman model DU spectrophotometer. The spectrophotometer is calibrated using ethyl xanthate since the absorbance of the xanthate group at this wave length is independent of the radical to which it is attached.

3

EXAMPLE I

Viscose containing 5% recoverable cellulose and 6.5% total alkali, calculated as sodium hydroxide, is prepared in the conventional manner using 60% carbon disulfide and a xanthation period of 4½ hours at 26° C. While mixing the viscose, sufficient polyethylene glycol, having an average molecular weight of 600, is added to give a concentration in the viscose of 0.2% by weight. The viscose is filtered, deaerated and ripened to a salt index of 26 and a viscosity of 42 poises. The viscose is then extruded into a coagulating and regenerating bath containing about 10.0% sulfuric acid, 9.5% zinc sulfate and 17.5% sodium sulfate, the bath being maintained at a temperature of 60° C. The yarn is passed for a distance of 20 inches through the primary coagulating and regenerating bath and then for a further distance of 15 inches through a hot secondary bath consisting of 2% sulfuric acid in water and maintained at a temperature of 95–97° C. The yarn is stretched 110% in the secondary bath by means of a power driven roller. After passing through the secondary bath the yarn is wound on a bobbin at a speed of 28 y.p.m. The yarn is subsequently purified, slashed and dried in the conventional manner. Part of the yarn, which has a denier of 1100, is twisted into 2-ply cord having a denier of 2450 for testing. The gel swelling and xanthate content of the yarn are determined as described above on samples of yarn taken just before the yarn passes into the hot secondary bath.

Properties of the yarn and cord are given in Table I, test A below. Test B of Table I shows the result obtained when test A is repeated except that 0.04% of nickel, in the form of the nickel-ethylenediamine tetraacetate complex, is added to the viscose during mixing. The nickel complex is formed by dissolving 286 g. "Tetrasodium Tetraene" (tetrasodium salt of ethylene diamine tetraacetic acid and 325 g. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in water and diluting to a volume of 2 liters. Test C shows the effect of omitting the coagulation modifier.

Table I

Test.....	A	B	C
Coagulation Modifier, percent.....	0.2	0.2	None
Nickel, percent.....	None	0.0	0.03
Xanthate Sulfur in yarn, percent.....	3.0	5.0	-----
Spinning Stretch, percent.....	110	152	121
Stretch at break, percent.....	140	180	-----
Gel Swelling.....	2.1	2.4	3.2
Yarn:			
Tenacity, g.p.d., dry.....	5.00	5.32	4.88
Tenacity, g.p.d., wet.....	3.84	4.09	2.60
Tenacity, g.p.d., loop.....	3.68	3.87	2.98
Cord:			
Tenacity, g.p.d., conditioned.....	4.39	4.62	3.34
Tenacity, g.p.d., oven dry.....	4.78	5.06	3.98

When the polyethylene glycol is replaced by a quaternary ammonium compound such as benzyltrimethylammonium hydroxide, substantially the same results are obtained.

EXAMPLE II

Viscose is prepared as in Example I except that the alkali content is 5.5% calculated as sodium hydroxide. The viscose is filtered, deaerated and ripened to a salt index of 23 and a viscosity of 21 poises. During the mixing operation sufficient triethanolamine is added to give a concentration of 0.05% by weight. Spinning is carried out as described in Example I except that the coagulating and regenerating bath contains 6.0% sulfuric acid, 6.0% zinc sulfate and 11.0% sodium sulfate.

Yarn and cord properties and other pertinent data are given in Table II. Test C shows the result obtained when no nickel is added to this viscose. Test D shows the improved results obtained when nickel is added to the viscose in the manner described in Example I.

4

Table II

Test.....	C	D
5 Coagulation Modifier, percent.....	0.05	0.05
Nickel, percent.....	None	0.06
Xanthate Sulfur in yarn, percent.....	3.8	4.5
Spinning Stretch, percent.....	98	138
Stretch at break, percent.....	-----	-----
Gel Swelling.....	2.11	2.26
Yarn:		
10 Tenacity, g.p.d., dry.....	4.91	5.21
Tenacity, g.p.d., wet.....	3.45	3.39
Tenacity, g.p.d., loop.....	3.56	3.70
Cord:		
Tenacity, g.p.d., conditioned.....	4.04	4.46
Tenacity, g.p.d., oven dry.....	4.67	4.73

15 The triethanol amine is replaced with hexamethylene diamine. The resulting yarns have substantially the same properties shown above.

EXAMPLE III

20 Modified viscose prepared as described in Example I is extruded into a coagulating and regenerating bath containing 9.0% sulfuric acid, 9.5% zinc sulfate and 17.5% sodium sulfate, the bath temperature being 60° C. In test E no nickel is added to the viscose. In tests F and G nickel is added to the viscose in the form of the nickel-ethylenediamine tetraacetate complex, in concentrations of 0.02 and 0.04%, respectively. The xanthate sulfur content of the yarn and the gel swelling is determined as described in Example I. The results shown in Table III illustrate the effectiveness of low concentrations of nickel in increasing the xanthate content of the yarn while the gel swelling is held at a low level.

Table III

Test.....	E	F	G
Nickel in viscose, percent.....	None	0.02	0.04
Xanthate sulfur in yarn, percent.....	3.0	8.7	9.4
Gel Swelling.....	2.0	2.12	2.04

40 When the polyethylene glycol of this example is replaced with an N-substituted dithiocarbamic acid such as sodium N-methylcyclohexyl dithiocarbamate, improved yarn properties are also obtained.

EXAMPLE IV

45 Modified viscose prepared as in Example I is extruded on a small scale into a coagulating and regenerating bath containing 9.85% sulfuric acid, 9.40% zinc sulfate and 17.35% sodium sulfate, the temperature of the bath being 60° C. The xanthate sulfur content and gel swelling of the filaments are determined after the filaments had traveled through the bath for a distance of 20 inches. The results shown in Table IV below illustrate the effectiveness of various nickel compounds in achieving the results of the present invention. The compounds are added to the viscose during the mixing operation except for the nickel sulfate which is added to the dilute sodium hydroxide solution, used to dissolve the xanthate, in the mixing tank prior to addition of the xanthate. When added in this manner the nickel sulfate reacts with the sodium hydroxide to give a finely dispersed precipitate of the hydroxide. On addition of the xanthate to the sodium hydroxide solution, the nickel hydroxide precipitate dissolves as evidenced by the absence of a precipitate in the viscose.

Table IV

Nickel in Viscose, Percent	Nickel Compound Added	Xanthate Sulfur, Percent	Gel Swelling
None	-----	2.8	2.18
0.057	Ethylenediamine complex.....	18.0	2.25
0.068	do.....	22.0	2.20
0.029	Ammonia Complex, Nickel Trithiocarbonate, Nickel sulfate.	14.6	2.10

5

The polyethylene glycol of this example is replaced with phenoxyethanol. Improved yarn properties similar to those above are obtained.

As mentioned previously the nickel may be added to the viscose in the form of any water-soluble compound. It is most conveniently added as a complex with compounds such as the sodium salt of ethylenediamine tetraacetic acid. This compound is sold commercially under the trade name "Versene" and under the trade name "Sequestrene". Other compounds which may be used to form nickel complexes are ethylenediamine, various ammonium compounds and sodium trithiocarbonate. Nickel trithiocarbonate may be readily formed by adding the nickel-ethylenediamine tetraacetate complex to a sodium trithiocarbonate solution; the sodium trithiocarbonate solution being prepared by reacting carbon disulfide with an aqueous sodium hydroxide solution.

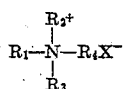
It has been observed that the nickel-ethylenediamine tetraacetate complex converts to the nickel trithiocarbonate complex when two solutions of these are mixed. In view of the fact that viscose contains appreciable quantities of sodium trithiocarbonate, it is believed that the nickel added to the viscose is substantially all converted to a nickel trithiocarbonate complex and that this accounts for the solubility of the nickel in spite of the presence of sulfide which would ordinarily be expected to precipitate the nickel. If, however, the nickel is added rapidly to the viscose in the form of a compound such as nickel sulfate or nickel chloride, then a substantial amount of the nickel will be precipitated as nickel sulfide and once precipitated in this form the nickel is not easily converted back to the trithiocarbonate complex. Therefore, if the nickel is added in the form of a compound other than a fairly stable complex, it is preferable to add the compound to the dilute sodium hydroxide solution used to dissolve the xanthate prior to addition of the xanthate. Under these conditions the nickel is so highly dispersed that it has opportunity to react with the trithiocarbonate in the xanthate crumb and thus prevent the precipitation of the nickel sulfide.

For effective results the nickel should be present in the viscose in a concentration of at least about 0.02% by weight of the viscose. High concentrations of nickel should be avoided since this leads to gel formation in the viscose. The maximum concentration employed is dependent on the composition of the viscose but it is preferred that it not exceed about 0.10%. In general, the range for most effective results is about 0.04 to about 0.10% nickel.

The coagulation modifiers which serve to reduce the gel swelling of the filaments, are generally present in relatively small amounts, about 0.1 millimole to about 10 millimoles per 100 grams of solution, preferably in the viscose solution. However, these compounds may be present in only the acid bath, or in both the acid bath and the viscose solution. When the coagulation modifier is added to both the viscose solution and the acid bath, it is generally desirable to maintain these same limits only basing the amount of the coagulation modifier on the total weight of the viscose solution and acid bath. A concentration exceeding these limits may, of course, be used but it seldom gives any further improvement in the product.

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



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

6

more than one phenyl radical, and where X⁻ is an anion having substantially no surface activity. The use of these compounds is disclosed in U.S. 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 U.S. 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, ethyldiethanolamine, 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' - diisobutylhexamethylene-diamine, 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 U.S. 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 dimethyldithiocarbamate, 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, 35% octadecenylamine 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. 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, butoxyethanol, phenoxyethoxyethanol, ethoxyethoxyethoxyethanol, butoxyethoxyethoxyethanol, phenoxyethoxyethoxyethanol, butoxyethoxyethoxyethoxyethanol, phenoxyethoxyethoxyethoxyethoxyethanol, 1 ethenyoxy-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 U.S. Patents 2,777,775; 2,792,278; 2,792,279; 2,792,280 and 2,792,281; British Patents 723,435; 730,451; 748,147 and 765,905, and French Patents 1,102,898 and 1,111,580.

In the process of this invention the viscose solution is prepared in the conventional manner. Alkali cellulose is first prepared by soaking sheets of wood pulp or cotton linters pulp in sodium hydroxide solution. The excess alkali is then drained and pressed from the saturated sheets. The resulting alkali cellulose is shredded and then aged to provide the desired viscosity in the prepared viscose. The shredded alkali cellulose is dropped into a rotatable drum called a barratte where xanthation occurs.

The alkali cellulose may be completely xanthated in the barratte or partially xanthated in the barratte and partially in the mixer. Splitting xanthation so that not over 90% is completed in the barratte is described in U.S. Patent 2,801,998, issued August 6, 1957, to A. Robertson. In either conventional or split xanthation, at least 30% carbon disulfide, based on the cellulose content of the alkali cellulose, should be used.

The xanthated or partially xanthated alkali cellulose is

now added to a tank where it is mixed with a measured quantity of dilute aqueous sodium hydroxide solution. The amount of sodium hydroxide solution is sufficient to provide a final viscose solution containing 4% to 9% cellulose or more and 4% to 9% or more total alkali calculated as sodium hydroxide. The standard viscoses of the industry, i.e., those having between 5% and 8% cellulose and between 5% and 7% alkali, are preferably used.

The viscose solution is filtered, deaerated and may be permitted to ripen at a temperature of about 18° C. to the desired salt index. While the process of this invention yields improved properties with ripe viscoses it is preferable to restrict ripening and spin the viscose in an unripened or a partially ripened state, i.e., salt indexes of 10 and higher.

The viscose may be extruded hot or cold. Heating may be accomplished by passing the viscose solution through a heat exchanger using hot oil, hot water, steam, or heated coagulating bath as the source of heat; or an electric heating unit may be inserted in the pipe.

The spinning bath is preferably maintained at a temperature between 40° C. and 80° C. and contains 4% to 10% sulfuric acid, 5% to 25% sodium sulfate and 3% to 15% zinc sulfate. If desired, other divalent metal salts known to reinforce or supplement the action of zinc sulfate may also be used. These include ferrous sulfate, manganese sulfate, nickel sulfate or chromic sulfate.

The filaments may be extruded through a spinning tube to confine the filaments in the critical stage of formation as described in U.S. Patent 2,440,057 to F. R. Millhiser. After extrusion, the filaments may travel through about 25 to 150 inches in the primary bath where they may be confined to a small area by means of a multiple roller set-up. The rollers are designed to apply tension to the traveling filaments in gradual increments and thereby orient them while they are still plastic. A preferred method is to apply a part of the stretch beyond the primary bath by passing the filaments through a secondary bath or shower located between two power driven rollers. The secondary bath may consist simply of water or of dilute (1% to 4%) sulfuric acid, or it may be diluted spinning bath at a temperature between 50° C. and 100° C. Total stretches of 80% or more are preferred for producing high tenacity yarns and as low as 30% may be acceptable for textile type yarns. From the last roller, the yarn may be wound on a bobbin or fed into a rotating bucket to form a cake and then washed and slashed. The slashing operation is well known and consists of stretching the yarn and applying a lubricating solution.

The yarns and cords of this invention have outstanding properties and may be used for any purpose where regenerated cellulose fibers are finding application, such as for reinforcement of rubber articles, automobile tires and in various textile fields.

Many other equivalent modifications will be apparent to those skilled in the art from a reading of the foregoing without a departure from the inventive concept.

What is claimed is:

1. In the process of producing a shaped structure of regenerated cellulose by extruding viscose into an acid-zinc sulfate bath in the presence of a coagulation modifier, the improvement which comprises adding at least about 0.02% by weight, based on viscose, of soluble nickel to the viscose prior to extrusion.

2. The process of claim 1 wherein the coagulation modifier is added to the viscose in amounts of from about 0.1 to about 10 millimoles per 100 grams of viscose.

3. The process of claim 1 wherein the soluble nickel is present in amounts of from about 0.04 to about 0.10% by weight based on the viscose.

4. The process of claim 2 wherein the soluble nickel is present in amounts of from about 0.04 to about 0.10% by weight based on the viscose.

5. The process of claim 4 wherein the coagulation

modifier is a polyethylene glycol having an average molecular weight of about 600.

6. The process of claim 4 wherein the coagulation modifier is triethanolamine.

7. The process of claim 4 wherein the acid-zinc sulfate bath is at a temperature of from about 40° C. to about 80° C.

8. As a composition of matter, viscose containing at least about 0.02% by weight, based on the viscose, of soluble nickel.

9. As a composition of matter, viscose containing from

about 0.04 to about 0.10% by weight, based on the viscose of soluble nickel.

References Cited in the file of this patent

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2,206,278	Dreyfus	July 2, 1940
2,412,969	Cramer	Dec. 24, 1946
2,535,044	Cox	Dec. 26, 1950
2,696,423	Dietrich	Dec. 7, 1954

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,879,170

March 24, 1959

Ivan Keith Miller

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 31, for "coagulations" read -- coagulation --; column 3, line 37, after "acid" insert a closing parenthesis; same column 3, in the table, in the column headed "B", second item, for "0.0" read -- 0.06 --; same table, first column thereof, last line, for "dry^o" read -- dry --; line 73, for "this" read -- the --; column 7, line 24, for "butoxyethanol" read -- butoxyethoxyethanol --; line 56, for British Patent No. "730,451" read -- 730,541 --.

Signed and sealed this 21st day of July 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents