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2,696,423

## VISCOSE MODIFIERS

Melvin Adam Dietrich, Claymont, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the reduction of the primary swelling of gel fibers from viscose and to the improvement of properties of regenerated cellulose articles by controlling the gel swelling during the manufacturing of the articles.

While known methods of reducing gel swelling are useful, it is desired to obtain still further improvements in yarn properties, for example, by better and more effective means of reducing gel swelling. An object of this invention is, accordingly, to provide a process of manufacturing regenerated cellulose filaments having very low gel swelling values and exhibiting considerably improved properties, particularly when twisted into cord. Another object is to provide a process of manufacturing regenerated cellulose yarn having entirely novel and desirable properties. Yet a further object is the provision of a new route to a high tenacity, highly fatigue-resistant regenerated cellulose fiber having a non-crenulated surface, and which gives high tenacity in twisted tire cord structures. A still further object is to provide new and highly effective modifiers. Other objects will appear hereinafter.

These objects are accomplished by adding to viscose preferably at least about 0.05% of a soluble salt of an N-substituted dithiocarbamic acid and extruding the resultant viscose into an acid coagulating bath containing about 1% to about 15% zinc sulfate and stretching the resultant filaments, preferably in a secondary hot bath. By "soluble salt of an N-substituted dithiocarbamic acid" is meant a salt of an N-substituted dithiocarbamic acid which dissolves in 6% aqueous sodium hydroxide to the extent of at least 0.05%. For this solubility, these modifiers should have no radical having more than 18 carbon atoms; those containing a radical having more are too insoluble. The preferred modifiers are mono- or di-N-substituted dithiocarbamates containing no radical of more than 10 carbon atoms and in which the nitrogen is attached to aliphatic carbon. The N-atom may be, then, a secondary or tertiary N-atom.

The invention will be more closely understood by reference to the examples and discussion which follow. These examples are given for illustrative purposes only and are not to be construed in any sense as limitative. The invention is generally applicable to the preparation of filaments, yarns, films, caps, bands, ribbons and other structures of regenerated cellulose but, for convenience, is discussed with particular reference to the production of viscose rayon yarn.

Gel swellings were determined in both yarn spun and films cast from the various viscoses. The numerical values of gel swelling given below for various yarn samples were all determined according to the following procedure. The gel yarn was collected from the first feed wheel without stretch and prior to the hot dip bath by allowing the yarn to drop onto a square of cheese cloth for 3 minutes. The sample was centrifuged (3600 R. P. M.) for 5 minutes and weighed in a closed bottle. The sample was washed free of acid, dried in an oven at 105° C. and weighed. The ratio of the gel weight to cellulose weight (grams of gel per gram of cellulose) is referred to as the gel swelling (yarn). Variations may be introduced in the procedure, e. g., in the stretch, spinning speed or length of bath travel, but these introduce only minor changes in the numerical values of yarn gel swelling.

An alternative method of determining gel swelling was 80 from films cast from the viscose. Films of modified

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and unmodified viscose, 15 mils. thick, cast on a glass plate, were coagulated in 8.5% sulfuric acid—17% sodium sulfate—10% zinc sulfate bath at 60° C. A sample of each coagulated film was cut from the center, blotted with absorbent pulp sheets and weighed. The weighed samples were then washed free of bath acid and salt, dried overnight at 105° C. and reweighed. Gel swellings (grams of gel film per gram of cellulose) were determined for both modified and unmodified films. The ratio of the gel swelling of the test item to the gel swelling of the unmodified viscose film was calculated. This numerical value was called the gel swelling ratio (films).

## Example 1

Viscose containing 0.15% of sodium cyclohexyl dithiocarbamate is prepared in the following manner using 5% cellulose and 6.5% total sodium hydroxide (5–6.5 viscose). Alkali cellulose aged to get the desired viscose viscosity (40 to 60 poises) is xanthated for 2½ hours using 43% CS<sub>2</sub> (based on air dry cellulose). Xanthate crumbs are dissolved in a solution of caustic containing the modifier in amounts to yield the concentration mentioned above. After mixing 3 hours at 17° C. the freshly prepared viscose is filtered while it is cold, deaerated and kept at 4° C. until spun, i. e., it is spun in the unripened state as shown by the high salt index value (16.0), high xanthate sulfur content (1.35%), and low sodium trithiocarbonate content (0.35%). In all examples the caustic content of 6.5% refers to the total alkalinity expressed as sodium hydroxide. It includes the free sodium hydroxide and that combined in the form of sodium carbonate, sodium trithiocarbonate, and sodium cellulose xanthate.

The viscose is spun into 1100 denier-720 filament yarn by extruding through a spinneret having holes of 0.0025" diameter into a primary coagulating and regenerating bath, comprising 9.5% H<sub>2</sub>SO<sub>4</sub>, 17% Na<sub>2</sub>SO<sub>4</sub>, and 10% ZnSO<sub>4</sub>. The yarn is given a bath travel of 41" by using a roller guide. The apparatus and general procedure used to extrude viscose into the bath and to collect the formed yarn are essentially the same as those used commercially in the so-called bobbin or spool-spinning process. The specific conditions include a bath temperature of 62° C., and a first feed wheel speed of 480 inches per minute. The filaments are carried through a 2% acid bath at 98° C. by a second feed wheel rotating at such a speed as to give 100% stretch beyond the first feed wheel. After stretching the yarn is held at constant length, either by multiple wraps about the second feed wheel or between the second and a third feed wheel, in such a manner that the yarn retains its stretched length for 50 to 100 inches, before collection at relatively low tension on a bobbin. The resulting regenerated gel yarn is washed free of acid and salt and then processed. The yarns are slashed while wet and twisted 3 turns per inch and tested after conditioning at 76° F. and 56% relative humidity for 48 hours. Some of the slashed yarn is also plied to a cord of 1100/2 construction, two strands of the 1100 denier yarn being combined to make the cord. The cords are then tested after being conditioned in a fashion similar to the yarn.

The properties of the yarn and cord from the viscose described herein are listed in Table I together for comparison with those of unripened, unmodified viscose.

TABLE I

	Unripened, unmodified	Unripened, modified
Bath Acid, percent.....	8.2	9.5
Yarn Properties:		
Tenacity, g./d., dry.....	4.66	4.90
Tenacity, g./d., wet.....	3.15	3.32
Tenacity, g./d., loop.....	3.51	3.83
Elongation, percent, dry.....	9.8	11.6
Elongation, percent, wet.....	17.6	24.6
Elongation, percent, loop.....	7.5	9.8
Gel swelling (yarn).....	2.79	2.22
Gel swelling ratio (film).....	1.0	.52
Cord Properties:		
Tenacity, g./d., conditioned.....	3.66	4.07
Tenacity, g./d., oven-dry.....	4.12	4.57

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The acidity of the spinning bath is an important factor in determining the gel swelling and resultant yarn and cord properties from any viscose, and modified viscoses generally require different acidities than do unmodified viscoses to obtain maximum properties. Selection of optimum acidity, of course, is a matter of simple experimentation for one skilled in the art. Spinning the unmodified, unripened viscoses at the acidities used for unripened, modified viscoses does not lead to the improved properties attained by the process of this invention.

The yarn produced by this and other examples has a number of properties which distinguishes it sharply from other regenerated cellulose yarn. The most readily apparent modifications are the unusual cross-section and surface features. For yarns prepared from unmodified viscose spun into a zinc bath, a skin or outer shell which swells to a different extent in water than that of the core is visible. These yarn cross sections show both deep and shallow crenulations around the contour of the filament. However, for yarns spun into zinc baths from viscose modified with the dithiocarbamate modifiers of this invention, the skin area is much greater, the boundary between the skin and core is very diffuse and the yarn has no appreciable crenulations so that the yarn has a relatively smooth surface. Such yarns are described also in the Cox patents, U. S. 2,536,014, 2,535,044 and 2,535,045, issued on December 26, 1950, on applications filed December 14, 1946, April 26, 1947, and April 26, 1947, respectively.

The fact that the filaments of the invention have smooth surface and considerably lower secondary swelling (water take-up by dried yarns) results in more resistance to fibrillating, laundering, and fatiguing than exhibited by normal crenulated viscose yarns.

## Example II

A 5-6.5 viscose (5% cotton linters cellulose—6.5% total sodium hydroxide) modified with 0.25% sodium amyl dithiocarbamate is prepared and spun in the manner described in Example I, using a 10.5% sulfuric acid, 17.0% sodium sulfate, 10% zinc sulfate coagulating and regenerating bath. The yarns are washed, slashed, and some of the yarn was plied to a cord of 1100/2 construction. Yarn and cord properties are given in Table II, along with those for a regular viscose control. It will be noted that the yarn from the modified, unripened viscose shows large improvements in cord strength and fatigue resistance of the cord over yarn produced from unripened, unmodified viscose spun under similar conditions.

TABLE II

	Unripened, unmodified	Unripened, modified
Bath Acid, Percent.....	8.2	10.5
Yarn Properties:		
Tenacity, g./d., dry.....	4.66	4.63
Tenacity, g./d., wet.....	3.15	2.55
Tenacity, g./d., loop.....	3.51	3.67
Elongation, percent, dry.....	9.8	12.3
Elongation, percent, wet.....	17.6	21.6
Elongation, percent, loop.....	7.5	10.2
Gel Swelling (yarn).....	2.79	2.31
Cord Properties:		
Tenacity, g./d., conditioned.....	3.66	4.13
Tenacity, g./d., oven-dry.....	4.12	4.42
Fatigue, minutes.....	119	545

## Example III

A 5-6.5 viscose (5% cotton linters cellulose—6.5% total sodium hydroxide) modified with 0.16% sodium butyl monoethanol dithiocarbamate is prepared and spun in the manner described in Example I, using an 8.5% sulfuric acid, 17.0% sodium sulfate, 10% zinc sulfate coagulating and regenerating bath. The yarns are washed, slashed, and a part of the slashed yarn plied to a cord of 1100/2 construction. Yarn and cord properties are given in Table III, along with those for a regular viscose control. It will be noted that the yarn from the modified, unripened viscose shows large improvements in cord strength and fatigue resistance of the cord over yarn produced from unripened unmodified viscose spun under similar conditions.

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TABLE III

	Unripened, unmodified	Unripened, modified
Bath Acid, Percent.....	8.2	8.5
Yarn Properties:		
Tenacity, g./d., dry.....	4.66	4.77
Tenacity, g./d., wet.....	3.15	3.33
Tenacity, g./d., loop.....	3.51	3.88
Elongation, percent, dry.....	9.8	12.9
Elongation, percent, wet.....	17.6	25.1
Elongation, percent, loop.....	7.5	10.3
Gel Swelling (yarn).....	2.79	2.13
Gel Swelling Ratio (film).....	1.0	0.38
Cord Properties:		
Tenacity, g./d., conditioned.....	3.66	4.10
Tenacity, g./d., oven-dry.....	4.12	4.39
Fatigue, minutes.....	119	349

## Example IV

A 5-6.5 viscose (5% cotton linters cellulose—6.5% total sodium hydroxide) modified with 0.06% sodium hexamethylene bis (dithiocarbamate) is prepared and spun in the manner described in Example I, using a 9.5% sulfuric acid, 17.0% sodium sulfate, 10.0% zinc sulfate coagulating and regenerating bath. The yarns are washed, slashed, and part of slashed yarn was plied to a cord of 1100/2 construction. Yarn and cord properties are given in Table IV, along with those for a regular viscose control. It will be noted that the yarn from the modified, unripened viscose shows large improvements in cord strength and fatigue resistance of the cord over yarn produced from unripened unmodified viscose spun under similar conditions, even though the dry yarn tenacity of the modified item is actually lower than that of the control. This may be attributed, in part, to the greatly improved elongations.

TABLE IV

	Unripened, unmodified	Unripened, modified
Bath Acid, percent.....	8.2	9.5
Yarn Properties:		
Tenacity, g./d., dry.....	4.66	4.05
Tenacity, g./d., wet.....	3.15	3.26
Tenacity, g./d., loop.....	3.51	3.40
Elongation, percent, dry.....	9.8	13.7
Elongation, percent, wet.....	17.6	26.1
Elongation, percent, loop.....	7.5	11.8
Gel Swelling (yarn).....	2.79	1.97
Gel Swelling Ratio (film).....	1.0	0.33
Cord Properties:		
Tenacity, g./d., conditioned.....	3.66	3.84
Tenacity, g./d., oven-dry.....	4.12	4.24
Fatigue, minutes.....	119	445

## Example V

A 5-6.5 viscose (5% cotton linters cellulose—6.5% total sodium hydroxide) modified with 0.3% potassium pentamethylene dithiocarbamate is prepared and spun in the manner described in Example I, using an 8.5% sulfuric acid, 17.0% sodium sulfate, 10.0% zinc sulfate coagulating and regenerating bath. The yarns are washed, slashed, and part of the yarn plied to a cord of 1100/2 construction. Yarn and cord properties are given in Table V, along with those for a regular viscose control. It will be noted that the yarn from the modified, unripened viscose shows a large improvement in cord strength over cords from yarn produced from unripened unmodified viscose spun under similar conditions.

TABLE V

	Unripened, unmodified	Unripened, modified
Bath acid, percent.....	8.2	8.5
Yarn Properties:		
Tenacity, g./d., dry.....	4.66	4.62
Tenacity, g./d., wet.....	3.15	3.25
Tenacity, g./d., loop.....	3.51	3.52
Elongation, percent, dry.....	9.8	13.5
Elongation, percent, wet.....	17.6	26.4
Elongation, percent, loop.....	7.5	10.4
Gel Swelling (yarn).....	2.79	2.20
Gel Swelling Ratio (film).....	1.0	0.71
Cord Properties:		
Tenacity, g./d., conditioned.....	3.66	4.08
Tenacity, g./d., oven-dry.....	4.12	4.48

It has been demonstrated in the foregoing examples that the dithiocarbamate modifiers markedly reduce gel swellings and that the reduction in gel swelling is accom-

panied by increases in yarn and cord properties. In particular, it has been shown that the modified yarns with low gel swelling give a much higher conversion of yarn strength to cord strength than do yarns from unmodified viscose.

Many other salts of dithiocarbamic acid are suitable modifying agents according to this invention, which is not limited to the specific examples cited previously. The effectiveness of a number of these dithiocarbamates can be shown by the reduction of gel swelling in films prepared from modified viscoses. Ten 5-6.5 viscoses are prepared as in Example I and modified with the agents shown in Table VI. Films are cast from the viscoses in the manner described previously and gel swelling ratios are determined. In this case the coagulating bath is 8.5% sulfuric acid, 17.0% sodium sulfate and 10.0% zinc sulfate. The gel swellings so obtained are much slower than for the accompanying control, from unmodified viscose, as shown by the gel swelling ratios in the table.

TABLE VI

Modifying Agent	Gel Swelling Ratio (Films)
None	1.00
0.58% sodium methyl dithiocarbamate	0.81
0.24% sodium benzyl dithiocarbamate	0.51
0.21% sodium ethylene bis (dithiocarbamate)	0.61
0.22% sodium 1,3-cyclohexane bis (dithiocarbamate)	0.30
0.46% sodium dibutyl dithiocarbamate	0.49
0.22% sodium dimethyl dithiocarbamate	0.57
0.27% sodium dioctyl dithiocarbamate	0.76
0.22% sodium lauryl dithiocarbamate	0.94
0.43% lithium cyclohexyl dithiocarbamate	0.81
0.30% sodium dithiocarbamates of the following mixture: 10% hexadecyl; 10% octadecyl; 35% octadecenyl; 45% octadecadienyl	0.84

In addition to the already named dithiocarbamates there are many others that can be used. Included among these additional modifiers are sodium hexamethylene bis (isobutyl dithiocarbamate); sodium ethylene bis (methyl dithiocarbamate); sodium 1,4-cyclohexane bis (ethyl dithiocarbamate); sodium xylylene bis (dithiocarbamate), and the like.

While the majority of the cited modifiers have been used as the sodium salt, the invention is not limited thereto. Any soluble salt of the dithiocarbamate may be used. Thus, the salt may be a sodium, lithium, potassium, ammonium or an amine salt. The preferred modifiers are the alkali 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.

The dithiocarbamate modifiers for effective results should be used in the viscose in concentrations of at least about 0.05% and, in general, it is unnecessary to use more than 0.75% of agent, a generally useful range being about 0.05 to 0.3% by weight of viscose. The optimum concentration of any given agent depends on its effectiveness, on its molecular weight, and on its stability. For example, larger concentrations of sodium dibutyl dithiocarbamate are needed than for sodium hexamethylene bis (dithiocarbamate). It also depends to some extent on process variables such as the spinning speed, since at high spinning speeds used in industrial practice, less agent is desired 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. Determination of the optimum concentration of the dithiocarbamate compound is a matter of simple experimentation for those skilled in the art.

As shown in the examples, the weighed amount of the modifier may be added to the caustic used in converting the xanthate crumbs to viscose or to already prepared viscose. It is obvious from this that the controlled weights of modifier could also be added to the cellulosic components being converted into viscose such as the cellulose, alkali cellulose or xanthate crumbs.

The dithiocarbamate modifiers may be used alone or in admixture with certain other compounds which augment the modification action and which in themselves may be modifiers. Such compounds include a number of other modifiers, such as, ethoxyethanol, butoxyethanol,

phenoxyethanol, methoxyethoxyethanol, butoxyethoxyethanol, phenoxyethoxyethanol, tetraethylene glycol dimethyl ether, diethylene glycol diethyl ether, ethylene glycol diethyl ether, triethylene glycol diethyl ether, tetramethylene glycol diethyl ether, triethylene glycol dimethyl ether and the like which exhibit solubility in 6% aqueous caustic soda to at least 1% and solubility in the coagulating bath not in excess of 0.5%. Also, polyethylene glycol having a molecular weight of from 300 to 1,000 more or less may also be mixed with the dithiocarbamates modified viscose of this invention to produce improved yarns or other regenerated cellulose structures. In some cases, a combination of three or more modifiers such as illustrated by Example VI that follows may be incorporated in the viscose and spun with excellent results.

## Example VI

A 5% cellulose-6.5% sodium hydroxide viscose is modified with 0.1% sodium cyclohexyl dithiocarbamate, 0.5% butoxyethanol and 0.2% polyethylene glycol (M. W.=300). The viscose preparation, spinning, yarn purification and slashing and yarn and cord testing were as specified in Example I. Dry tenacity of the yarn is about 4.9 g./d. and the cord tenacity is about 4.2 g./d. as compared with 4.6 g./d. and 3.6 g./d. for unmodified yarn and cord respectively.

The viscose used in the process of the invention may be a variety of types; for example, it may be from wood pulp, cotton linters, mixtures of the two, or even other types of cellulose. The composition of the viscose may also be varied widely. For example, it may have a cellulose content of from 4% to 10% or even more and an alkali content of from 4% to 9% or more. The standard viscoses of the industry, i.e., those having between 5% and 7% cellulose and between 4% and 7% alkali, are preferably used. The amount of carbon disulfide used in xanthation can be from 25% to 50% (based on the recoverable bone-dry cellulose). It has been found that higher than normal xanthate sulfur contents (higher salt indices) can be used in the viscose when the dithiocarbamates described herein are added and there appears to be an advantage in stretchability and level of yarn properties if salt indices higher than 5 are used. It is necessary to use 30% or greater amounts of carbon disulfide to obtain salt indices of 5 or over in unripened viscoses.

While the use of unripened viscose is of special interest in the process of this invention, it can be shown that considerable improvements in gel swelling are also obtained with normally ripened viscose, thus demonstrating that the process is directly applicable to existing plant practice. For example, a 7-6 viscose containing 32% CS<sub>2</sub> and 0.25% sodium cyclohexyl dithiocarbamate is prepared. In this case, however, the viscose is ripened as is done for normal viscose to a salt index of 4.5 (xanthate sulfur 1.05%). Films are cast from the viscose in the manner described previously and gel swellings are determined. In this case the coagulating bath is 8.9-17-10 (H<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-ZnSO<sub>4</sub>). The gel swelling so obtained is 88% of that of an accompanying control from unmodified viscose.

The spinning baths suitable for use in the invention contain sulfuric acid and zinc sulfate. Zinc sulfate is an essential component of the spinning bath since, in its absence, the dithiocarbamate compounds have no effect on spinning and yarn properties. Sodium sulfate is usually present but is not essential. If desired, additional salts of divalent metals known to reinforce or supplement the action of zinc sulfate may be used, such as ferrous sulfate, manganese sulfate, or nickel sulfate, particularly the first-named salt. The use of these divalent metal salts makes it possible to use smaller amounts of zinc sulfate than are necessary in their absence. Preferably, the spinning bath contains from 4% to 12% of sulfuric acid, from 13% to 25% of sodium sulfate, and from 1% to 15% of zinc sulfate, optionally with 1% to about 5% ferrous sulfate. The optimum quantity of zinc sulfate from the standpoint of practical spinning speeds, reduction in gel swelling, and extent of modification of physical properties of yarn appears to be 3% to 10%. The foregoing examples have demonstrated the marked reduction in gel swelling caused by the spinning of 5-6.5 viscoses containing dithiocarbamates into 10% zinc sulfate baths. Similarly, films cast from 5-6.5 viscose

modified with 0.21% sodium cyclohexyl dithiocarbamate, will give a gel swelling only 57% of that from an accompanying control from unmodified viscose when both are cast in an 8.5%  $\text{H}_2\text{SO}_4$ —22%  $\text{Na}_2\text{SO}_4$ —5%  $\text{ZnSO}_4$  bath. With the addition of dithiocarbamates to viscose, it is possible to obtain excellent yarns in the upper range of bath acidity under which conditions normal unmodified viscoses give yarns of decreased quality. The temperature range of best spinnability is from 40° C. to 75° C. On the basis of available data, it is desirable to have the bath acidity as low as is practical for a given spinning speed in order to get optimum filament structure and yarn properties. Each of the above concentrations should be adjusted to each other and to the composition of the viscose. It is desirable to use as high a total solids content as possible in the coagulating bath to give the highest degree of gel shrinkage and improved stretchability.

The filaments may be given a long travel of 130 to 250 inches in the primary bath by means of a multiple roller setup which gradually applies tension to the traveling filaments and thereby orients them while they are still plastic. The preferred method, however, is to apply a part or all of the stretch beyond the primary bath in a secondary bath or to use a combination of air and hot bath stretch. The secondary bath may consist simply of water or of dilute (1% to 3%) sulfuric acid, or it may have the same composition as the coagulating bath but at a greater dilution, e. g., one-fourth of the concentration of the coagulating bath. The thread can be given a travel of 10 to 50 inches in the secondary bath of hot water or dilute bath. The temperature of the secondary bath is preferably between 50° C. and 100° C. Stretches of 80% to 100% are preferred for producing high tenacity yarn and 20% to 30% for textile type yarns. When using the two-bath spinning system, the preferred procedure is to draw off the freshly coagulated gel yarn with a feed wheel speed equal to or less than the jet velocity and to apply all of the stretch between positively driven rollers traveling at different speeds. The amount of stretch applied depends on the properties desired for the yarn. The bobbin process has been used in the example, but it is immaterial whether spinning is by bobbin, bucket, or continuous processes. The yarn cake is washed free of acid and salt and then dried under tension. If preferred, it may be twister- or slasher-dried to enable the dry elongation of the finished product to be controlled.

Spinning may be carried out with the aid of spinning tubes such as described in Millhiser U. S. Patent 2,440,057 or Drisch et al. U. S. Patent 2,511,699. These tubes of relatively small diameter and of substantial length confine the bath and filaments in their critical stage of formation so that no substantial tension is imposed on the filaments because the speed of concurrent bath flow is maintained only slightly below the speed of the filament bundle passing through the tube. It is thus possible to materially increase the rate of spinning over methods earlier described without substantially sacrificing the desirable properties set forth above.

The novel and improved yarns obtainable through the process of this invention can, in general, be used instead of regular regenerated cellulose fibers for any purpose where the latter are finding applications, more particularly in the textile and tire cord industries. The production of yarns having smooth (non-crenulated) surfaces is highly advantageous, for such yarns have very high strength and improved soil and abrasion resistance. The combination of high tenacity and high fatigue resistance represents a material advance and a new type of regenerated cellulose article.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

I claim:

1. A process for the production of regenerated cellulose articles which comprises adding to viscose a soluble salt of an N-substituted dithiocarbamic acid and extruding the resultant viscose into an acid coagulating bath containing about 1% to about 15% zinc sulfate.

2. A process in accordance with claim 1 in which said dithiocarbamate is sodium cyclohexyl dithiocarbamate.

3. A process in accordance with claim 1 in which said dithiocarbamate is sodium amyl dithiocarbamate.

4. A process in accordance with claim 1 in which said

dithiocarbamate is sodium butyl monoethanol dithiocarbamate.

5. A process in accordance with claim 1 in which said dithiocarbamate is sodium hexamethylene bis (dithiocarbamate).

6. A process in accordance with claim 1 in which said dithiocarbamate is sodium benzyl dithiocarbamate.

7. A process in accordance with claim 1 wherein the amount of zinc sulfate is from about 3% to about 10%.  
8. A process in accordance with claim 1 in which the said acid bath contains about 4% to about 12% sulfuric acid and about 13% to about 25% sodium sulfate.

9. A process in accordance with claim 1 in which the said acid bath contains about 4% to about 12% sulfuric acid, about 13% to about 25% sodium sulfate and about 1% to about 5% ferrous sulfate.

10. A process for the production of regenerated cellulose articles which comprises adding to viscose a soluble salt of an N-substituted dithiocarbamic acid containing no radical containing more than 18 carbon atoms and extruding the resultant viscose into an acid coagulating bath containing about 1% to about 15% zinc sulfate.

11. A process in accordance with claim 8 in which the said dithiocarbamic acid contains no radical having more than 10 carbon atoms.

12. A process for the production of regenerated cellulose articles which comprises adding to viscose up to about 0.5% of a soluble salt of an N-substituted dithiocarbamic acid and extruding the resultant viscose into an acid coagulating bath containing about 1% to about 15% zinc sulfate.

13. A process for the production of regenerated cellulose articles which comprises adding to viscose up to about 0.5% of a soluble salt of an N-substituted dithiocarbamic acid and regenerating the resultant viscose by extruding it into an acid bath containing about 1% to about 15% zinc sulfate, thereby reducing the gel swelling ratio of the resultant gel structure to less than 1.0.

14. A process for the production of regenerated cellulose structures which comprises extruding into an acid coagulating bath viscose containing a measured amount of a salt of an N-substituted dithiocarbamic acid which salt is soluble in 6% aqueous sodium hydroxide to the extent of at least about 0.05%, said bath containing about 1% to about 15% zinc sulfate.

15. A process for the production of regenerated cellulose articles which comprises adding to viscose an alkali-metal salt of an N-substituted dithiocarbamic acid and extruding the resultant viscose into an acid coagulating bath containing about 1% to about 15% zinc sulfate.

16. A process for the production of regenerated cellulose articles which comprises adding to viscose about 0.05% to about 0.5% of a soluble salt of an N-substituted dithiocarbamic acid; extruding the resultant viscose into an acid coagulating bath containing about 1% to about 15% zinc sulfate; and stretching the resultant formed article about 20% to about 100% during spinning.

17. A process for the production of regenerated cellulose articles which comprises adding to viscose about 0.05% to about 0.5% of a soluble salt of an N-substituted dithiocarbamic acid and extruding the resultant viscose into an acid coagulating bath maintained at 40° C. to 75° C. which contains about 4% to about 12% sulfuric acid, about 13% to about 25% sodium sulfate and about 3% to about 10% zinc sulfate.

18. A process in accordance with claim 1 wherein said N-substituted dithiocarbamic acid contains a cyclohexyl group attached to said nitrogen (N) atom.

19. A process in accordance with claim 1 wherein said N-substituted dithiocarbamic acid is a mono-N-substituted dithiocarbamic acid.

20. A process in accordance with claim 1 wherein said N-substituted dithiocarbamic acid is a di-N-substituted dithiocarbamic acid.

21. A process in accordance with claim 20 wherein said disubstituted dithiocarbamic acid contains a methyl group attached to the nitrogen atom.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

Number	Name	Date
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