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SPINNING OF VISCOSE
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Fig. 1.



Fig. 2.



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SPINNING OF VISCOSE

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This invention relates to the regeneration of cellulose from viscose. More particularly it relates to a new process for manufacturing regenerated cellulose articles such as filaments or films having improved properties.

Although the invention is generally applicable to the preparation of filaments, yarns, films, caps, bands, ribbons, and other structures of regenerated cellulose, it will be discussed with particular reference to the production of viscose rayon yarn.

It is known that the general strength and quality of viscose yarns are improved through reduction of the primary swelling of the gel fibers. The great importance of the gel swelling factor in viscose spinning operations has attained full recognition only in the last few years (see, for example U. S. 2,347,883 and 2,347,884). It is now recognized that, to constitute a commercially useful viscose rayon process, the viscose composition and the composition of the sulfuric acid coagulating bath must be so balanced as to permit the production of regenerated cellulose filaments having a gel swelling factor of not more than about 6.5. It has been found that, for a given viscose, yarn properties such as tenacity, elongation, softness, etc., are, as a rule, best when spinning is done at or near the point of minimum gel swelling. It has been found, moreover, that yarn properties are improved through methods designed to reduce the gel swelling factor below the above-mentioned value of 6.5 and that, in general, the greater the reduction, the more marked the improvements. Already proposed methods of reducing the gel swelling factor include the addition to the coagulating bath of zinc sulfate or of ferrous, manganous, or chromic sulfates (U. S. Patents 2,364,273; 2,347,883; and 2,347,884). While these methods represent valuable advances in the art, further improvements in yarn properties are needed.

It is well known that unripened viscoses, i. e., viscoses of salt index of about 7 or higher, are not suitable for spinning by the methods currently used in the industry with normally ripened viscoses, i. e., viscoses of salt index of about 5 to 6 or lower. This is attributed to the high primary gel swelling of yarns from green viscoses, even though the high degree of xanthation of green viscoses (which is reflected in proportionately

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high salt index values) has been thought desirable on theoretical grounds for viscose spinning. A further problem, then, is to make unripened viscose (the so-called "green viscose") amenable to spinning. This is highly desirable since the use of unripened viscose would result in decreasing or eliminating the ripening time now necessary in manufacturing practice. Accordingly, methods for further reducing the gel swelling factor of unripened viscose, and in particular, methods involving further improvements in yarn properties are particularly desirable.

An object of this invention is to provide a process of manufacturing regenerated cellulose filaments having gel swelling values lower than heretofore attainable and exhibiting considerably improved yarn properties. Another object is to provide a process whereby unripened viscose can be spun in conventional spinning equipment to give yarn of high quality. A further 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 high tenacity, highly fatigue-resistant regenerated cellulose fiber having a non-crenulated surface and having improved soil and abrasion resistance. Other objects will appear hereinafter.

These objects are accomplished, in accordance with the invention, by extruding viscose into a sulfuric acid-sodium sulfate coagulating bath containing zinc sulfate and stretching the filaments, preferably in a secondary bath, said viscose containing dissolved therein at least 1 millimole per 100 grams of viscose of a monoamine soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%, the said monoamine having at least four carbon atoms but containing no radical of more than six carbons.

Another object, which was unexpectedly found possible to accomplish through the invention described below was the production of very high strength yarns having smooth (non-crenulated) surfaces with improved soil resistance and abrasion resistance. The combination of high tenacity and high fatigue resistance with smooth surface had not heretofore been achieved.

The use of certain secondary and tertiary amines in spinning baths or in viscose for preventing or reducing incrustation of spinnerets

is known (Br. 533,309). However, the solubility in viscose of the agents disclosed is much too low (less than 0.1%) to cause a detectable reduction of the gel swelling. There was, therefore, no reason to expect that the alkali-soluble amine modifiers of this invention would have any effect whatever on viscose spinning and/or yarn properties, and even less reason to expect that their use would decrease gel swelling of the yarn below any previously known minimum and permit production, from either ripened or unripened viscose, of high tenacity filaments possessing certain entirely new properties.

By the term "alkali-soluble monoamine modifiers" is meant those monoamines having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to an extent of at least 0.3%.

Referring to the drawings;

Figure 1 is a dyed cross section of a filament regenerated from unripened, unmodified viscose, and

Figure 2 is a dyed cross section of a filament regenerated from viscose unripened, modified with the agents of and by the processes of this invention.

The invention will be more clearly understood by referring to the examples and discussion which follow. These examples are given for illustrative purposes and are not to be construed in any sense as limitative. The numerical values of gel swelling given below for various yarn samples were all determined according to the following procedure. The gel thread was collected in a mono-layer on a bobbin, by manually operating a traverse mechanism with the thread being stretched 80% in the hot dip bath. The sample was centrifuged (1400 R. P. M.) for a minute, cut off, 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. 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 gel swelling.

Another important indication of yarn quality is the factor referred to below as "D" value. This factor relates to the rate of neutralization of the viscose filament in the coagulating and regenerating bath. It is determined by adding to the viscose a suitable indicator, in this case bromocresol purple (pH range 5.2 to 6.8), and observing the distance in inches from the spinneret at which the purple color completely disappears in the traveling filament. This distance is the "D" value. The selected amines suitable for use in this invention reduce the rate of neutralization of the spinning filaments, hence increase the "D" value over that of unmodified viscose. It has been found that, in general, the greater the "D" value, the better the yarn properties. The increased "D" value is believed to indicate that the modifying agents of this invention permit greater dehydration of the viscose before the gel structure of the filament is permanently set.

Example I

Viscose containing 1.8 millimoles of triethanolamine per 100 grams of viscose is prepared in the following manner using 7% cellu-

lose and 6% total sodium hydroxide (7-6 viscose). Alkali cellulose aged to get the desired viscose viscosity (40 to 60 poises) is xanthated for 2½ hours using 35% CS₂ (based on the recoverable bone-dry cellulose). Xanthate crumbs are dissolved in a solution of caustic containing the modifier in amounts mentioned above. After mixing 1½ hours at 0° C., the freshly prepared viscose is filtered while it is cold, deaerated, and kept at 0° C. until spun, i. e., it is spun in the unripened state, as shown by the high salt index values, high xanthate sulfur content, and low sodium trithiocarbonate content. In all examples, the caustic content of 6% refers to the total alkalinity expressed as sodium hydroxide. It includes the amine modifier and the free sodium hydroxide, and that combined in the form of sodium carbonate, sodium trithiocarbonate, and sodium cellulose xanthate.

The viscose is spun into 275 denier-100 filament yarn by extruding through a spinneret having holes of 0.0025-inch diameter into a primary coagulating and regenerating bath comprising 6.0% H₂SO₄, 14% Na₂SO₄, and 15% ZnSO₄. The yarn is given a bath travel of 28 inches by using a roller guide. The apparatus and general procedure used to lead viscose into the bath and to collect the formed thread are essentially the same as those used commercially in the so-called bobbin or spool process. The specific conditions include a bath temperature of 50° C. and a first feed wheel speed of 485 inches per minute. The filaments are carried through a water bath at 95° C. to 100° C. and wound up at such a speed as to give 80% stretch beyond the feed wheel. The resulting regenerated gel yarn is washed free of acid and salt and then processed. The yarns which are dried on the bobbin or, alternately, partially relaxed before drying by re-winding on another bobbin, are twisted 4 turns per inch and tested after conditioning at 21° C. and 60% relative humidity for 48 hours.

The properties of the yarn prepared from the viscoses described herein are listed in the accompanying table together, for comparison, with those of unripened, unmodified viscose and of ripened, unmodified viscose (the standard viscose of commercial operation), both controls being spun under conditions identical to those for the modified viscoses. It will be seen that the gel swelling value is lowest and the "D" value highest for the modified viscose. The physical properties, especially dry and wet tenacity, are higher than those for controlled viscoses.

The yarn produced by this and other examples has a number of properties which distinguishes it sharply from other regenerated cellulose yarn. Its properties are similar to those produced through modification of viscose with short-chain quaternary ammonium compounds which are described and claimed in copending application Serial No. 716,415. The most readily apparent modifications are the new 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 amine modifiers of this invention, the boundary between the skin and core is very diffuse and crenulations are absent giving the yarn a smooth surface. The differences in cross-sections between modified

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and unmodified yarns spun under identical conditions are shown in the accompanying drawings in Figure 1 and Figure 2.

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, fatiguing and soiling action than exhibited by normal crenulated viscose yarns.

Yarn Properties	Unripened, modified	Unripened, unmodified	Ripened, unmodified
Ten., g./d., dry.....	3.94	3.55	3.45
Ten., g./d., wet.....	2.89	2.0	2.20
Ten., g./d., loop.....	2.54	2.8	1.93
Elong., percent dry.....	6.7	7.7	8.0
Elong., percent wet.....	24.6	18.6	21.3
Elong., percent loop.....	3.4	5.2	4.1
Gel swelling.....	2.5	3.1	3.46
"D" value, in.....	3.7	1.5	1.5

Example II

A 7-6 viscose modified with 3.0 millimoles of triethylamine per 100 grams of viscose is prepared and spun in the manner described in Example I. In this case, however, the coagulating bath is 9-23-4 ($\text{H}_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--ZnSO}_4$). The yarn properties are tabulated below along with those of green, unmodified and ripened, control viscose. It will be noted that the use of unripened, modified viscose gives lower gel swelling, lower rate of neutralization (higher "D" value), and improved yarn properties.

Yarn Properties	Unripened, modified	Unripened, unmodified	Ripened, unmodified
Ten., g./d., dry.....	3.74	3.65	3.40
Ten., g./d., wet.....	2.53	2.13	2.20
Ten., g./d., loop.....	2.53	2.57	2.16
Elong., per cent Dry.....	5.8	6.2	5.6
Elong., per cent wet.....	20.3	15.7	18.0
Elong., per cent loop.....	3.2	3.6	3.0
Gel swelling.....	2.9	3.3	3.2
"D" value, in.....	4.0	2.5	2.0

Example III

A cotton linters viscose containing 7% cellulose, 6% sodium hydroxide, and 2.9 millimoles of diethanolamine per 100 grams of viscose is prepared and spun as described in Example I. Yarns with smooth surface and improved physical properties (see table below) were obtained.

Yarn Properties	Unripened, modified	Unripened, unmodified
Ten., g./d., dry.....	3.75	3.40
Ten., g./d., wet.....	2.47	2.20
Ten., g./d., loop.....	2.56	2.16
Elong., per cent dry.....	5.7	5.6
Elong., per cent wet.....	15.5	18.0
Elong., per cent loop.....	3.2	3.0
Gel swelling.....	2.76	3.2
"D" value, in.....	3.3	2.0

Example IV

A cotton linters viscose containing 7% cellulose, 6% caustic, and 1.9 millimoles of butylmonolamine per 100 grams of viscose is prepared as described in Example I. The viscose is spun in an unripened state in a sulfuric acid-sodium sulfate-zinc sulfate (10-23-4) bath and all conditions of Example I for spinning and processing are used. Yarns with smooth surface are obtained. The marked lowering of gel swelling

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and improvement in wet strength are shown in the table below.

Yarn Properties	Unripened, modified	Unripened, unmodified
Ten., g./d., dry.....	3.86	3.65
Ten., g./d., wet.....	2.49	2.13
Ten., g./d., loop.....	2.45	2.57
Elong., per cent dry.....	6.6	7.1
Elong., per cent wet.....	17.4	16.7
Elong., per cent loop.....	3.4	4.3
Gel swelling.....	2.6	3.2
"D" value, in.....	6.0	2.5

Example V

An unripened 7-6 viscose containing 2.5 millimoles of diethylaminoethanol is spun into a 9-23-4 ($\text{H}_2\text{SO}_4\text{--Na}_2\text{SO}_4\text{--ZnSO}_4$) bath and the yarn is stretched and processed as in Example I. The reduction in gel swelling and neutralization rates (increased "D" value) and improved yarn properties of the non-crenulated fibers thus obtained are shown in the table below.

Yarn Properties	Unripened, modified	Unripened, unmodified
Ten., g./d., dry.....	3.92	3.85
Ten., g./d., wet.....	2.68	2.16
Ten., g./d., loop.....	2.36	2.89
Elong., percent dry.....	6.5	7.1
Elong., percent wet.....	17.6	16.7
Elong., percent loop.....	3.5	4.3
Gel swelling.....	2.55	3.2
"D" value, in.....	6.0	2.5

Example VI

A cotton linters viscose containing 7% cellulose, 6% total caustic, and 1.8 millimoles of triethanolamine per 100 grams of viscose is prepared and ripened to a salt index of 5.0 as is normally done in commercial production and then spun into filaments using all conditions of Example I for collection and processing with the exception that an 8-23-4



bath instead of an 8-14-15 was used. A considerable decrease in gel swelling and increase in "D" value are obtained which are reflected in a measurable increase in physical properties of the yarn (table below). The character of the filament is changed in the same manner as noted with unripened viscoses.

Yarn Properties	Ripened, modified	Ripened, unmodified
Ten., g./d., dry.....	3.42	3.26
Ten., g./d., wet.....	2.41	2.21
Ten., g./d., loop.....	2.33	2.45
Elong., percent dry.....	6.4	6.4
Elong., percent wet.....	23.1	21.1
Elong., percent loop.....	3.9	3.9
Gel swelling.....	2.7	3.1
"D" value, in.....	4.0	2.5

Example VII

A7-6 viscose modified with 3.5 millimoles of cyclohexylamine per 100 grams of viscose is prepared and spun and the yarns are processed in the manner described in Example I. In this case, however, the coagulating bath is 8-23-4



As may be seen in the table below the wet strength is better than for the accompanying control and

the rate of neutralization and gel swelling are much lower.

Yarn Properties	Unripened, modified	Unripened, unmodified
Ten., g./d., dry	3.83	3.90
Ten., g./d., wet	2.74	2.17
Ten., g./d., loop	2.80	2.96
Elong., per cent dry	6.2	7.1
Elong., per cent wet	20.1	17.1
Elong., per cent loop	3.9	4.7
Gel swelling	2.49	3.23
"D" value, in.	7.0	3.0

Example VIII

A cotton linters viscose containing 7% cellulose and 6% sodium hydroxide and 4.5 millimoles of *n*-amylamine per 100 grams of viscose is prepared as described in Example I. The viscose is spun in an unripened state in 8-23-4



bath and all conditions of Example I for spinning and processing are used. The table below shows the improvement in loop and wet tenacities and gel swelling obtained from this modifier.

Yarn Properties	Unripened, modified	Unripened, unmodified
Ten., g./d., dry	3.52	3.63
Ten., g./d., wet	2.62	2.11
Ten., g./d., loop	2.98	2.66
Elong., per cent dry	6.7	8.1
Elong., per cent wet	21.3	20.0
Elong., per cent loop	4.5	5.4
Gel swelling	2.62	3.26
"D" value, in.	5.5	2.5

The modifying agents suitable for the purpose of this invention are primary, secondary, and tertiary monoamines which are soluble to at least 0.3% in 6% aqueous sodium hydroxide. The solubility requirement is essential since it has been found that emulsions in viscose of alkali-insoluble amines are ineffective for the purpose of this invention. Complete solubility is required. It is not feasible to state the necessary solubility in terms of viscose as the solvent since viscose composition, hence solvent power, varies rather widely. However, any amine soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% is suitable, provided it also fulfills the other conditions previously stated, namely

(a) It must be a monoamine. It has been found that certain diamines, e. g. ethylene diamine have practically no effect as regards decrease in gel swelling and increase in "D" value.

(b) It must have at least four carbon atoms. Lower amines such as methylamine or ethylamine are substantially ineffective.

(c) It must have no radical of more than six carbon atoms. Larger radicals, in addition to decreasing the solubility of the amine, tend to produce surface-activity which is not desirable in the process of this invention.

The preferred modifiers are those in which the amino nitrogen is attached to hydrocarbon groups, preferably alkyl groups, and/or to hydroxyalkyl groups.

An obvious requirement besides solubility is that modifiers must be substantially chemically inert and unaffected by components of the viscose before coagulation. Suitable agents which may be mentioned in addition to those used in the examples are diethylamine, dipropylamine, butyl-

amine, ethyldiethanolamine, dipropanolamine, propylpropanolamine, hexanolamine, amyldiethanolamine, butylmethylethanolamine, propylethanolamine, cyclohexylethanolamine, hexamethyleneimine, piperidine, pyridine, and hexyldiethanolamine.

The amine modifiers for effective results should be used in the viscose in concentrations of at least 1.0 millimole of agent per 100 grams of viscose, and, in general, it is unnecessary to use more than 10 millimoles of agent per 100 grams of viscose, a generally useful range being 1.0 to 4.0 millimoles per 100 grams of viscose. In terms of the less informative weight percent basis there should be used between 0.1 and 1.0% of the modifying agent. The optimum concentration of any given agent depends on its effectiveness and on its molecular weight. For example, larger concentrations of diethylamine are needed than for triethylamine. 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 amine compound is a matter of simple experimentation for those skilled in the art.

The viscose used in the process of the invention may be of 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 8% or more. The standard viscoses of the industry, i. e., those having between 5% and 7% cellulose and between 4% and 6% 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 amines 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. Thus, one of the chief advantages of the invention is that unripened or partially ripened viscoses may be used, with the result that the ripening time and space now required in viscose plants may be eliminated or substantially reduced.

While the use of unripened viscose is of special interest in the process of this invention, it has been shown (Example VI) that notable improvements in yarn quality are also obtained with normally ripened viscose, thus making the process directly applicable to existing plant practice.

The spinning baths suitable for use in the invention contain sulfuric acid, sodium sulfate, and zinc sulfate. Zinc sulfate is an essential component of the spinning bath since, in its absence, the amine compounds have no effect on spinning and yarn properties. 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, nickel sulfate, or chromic sulfate, par-

ticularly 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 2% to 15% of zinc sulfate, optionally with 1% to about 5% of 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 5%. With the addition of amines 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 65° C. On the basis of available data, it is desirable to have the bath acidity and temperature 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 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. 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. 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 thread can be given a travel of 10 to 50 inches in the secondary bath of hot water or dilute bath. As mentioned above, the amount of stretch applied depends on the properties desired for the yarn.

On the basis of available data, it is thought probable that the mechanism by which amine compounds influence the spinning process is through interaction with zinc sulfate on the one hand and with the sodium trithiocarbonate of the viscose on the other hand. It has not yet been possible to determine whether this effect on filament formation is accomplished through (1) buffer action, (2) transient formation of insoluble complexes, which might exercise some control on the porosity of the initial skin which is set up, or (3) other colloidal effects.

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.

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 method of producing regenerated cellulosic structures which comprises spinning viscose containing at least one millimole per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate.

2. A method of producing regenerated cellulosic structures which comprises spinning viscose containing from about 1 to about 4 millimoles per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate.

3. In a method of producing regenerated cellulosic structures by extruding viscose in an aqueous sulfuric acid bath containing from 1% to 15% zinc sulfate, the step which comprises incorporating in the said viscose at least 1 millimole per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

4. A method of producing regenerated cellulosic structures which comprises the steps of spinning viscose containing at least one millimole per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate; passing said structures into a second bath and stretching said structures to an extent of at least 20%.

5. A process of producing regenerated cellulosic structures which comprises incorporating in viscose at least 1 millimole per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%, extruding the resultant viscose into a coagulating bath comprising an aqueous solution of 4% to 12% sulfuric acid, 13% to 25% sodium sulfate, and 1% to 15% zinc sulfate.

6. A process as defined in claim 5 in which the said structures are passed into a second bath and stretched to an extent of at least 20%.

7. Viscose containing at least 1 millimole per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

8. Viscose having a salt index of at least 5 and containing at least one millimole per 100 grams

of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

9. Viscose containing 4% to 10% cellulose combined as sodium cellulose xanthate with from 25% to 50% carbon disulfide, 4% to 8% of sodium hydroxide and at least one millimole per 100 grams of viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

10. A method of producing regenerated cellulosic structures which comprises spinning unripened viscose containing at least one millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate.

11. A method of producing regenerated cellulosic structures which comprises spinning unripened viscose containing from about 1 to about 4 millimoles per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate.

12. In a method of producing regenerated cellulosic structures by extruding unripened viscose in an aqueous sulfuric acid bath containing from 1% to 15% zinc sulfate, the step which comprises incorporating in the said unripened viscose at least 1 millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

13. A method of producing regenerated cellulosic structures which comprises the steps of spinning unripened viscose containing at least one millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3% in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate; passing said structures into a second bath and stretching said structures to an extent of at least 20%.

14. A process of producing regenerated cellulosic structures which comprises incorporating in unripened viscose at least 1 millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but con-

taining no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%, extruding the resultant unripened viscose into a coagulating bath comprising an aqueous solution of 4% to 12% sulfuric acid, 13% to 25% sodium sulfate, and 1% to 15% zinc sulfate.

15. A process as defined in claim 14 in which the said structures are passed into a second bath and stretched to an extent of at least 20%.

16. Unripened viscose containing at least 1 millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

17. Unripened viscose having a salt index of at least 5 and containing at least one millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

18. Unripened viscose containing 4% to 10% cellulose combined as sodium cellulose xanthate with from 25% to 50% carbon disulfide, 4% to 8% of sodium hydroxide and at least one millimole per 100 grams of unripened viscose of an aliphatic monoamine having at least four carbon atoms but containing no radical of more than six carbon atoms and being soluble in 6% aqueous sodium hydroxide to the extent of at least 0.3%.

19. A method in accordance with claim 1 in which the said monoamine is n-amylamine.

20. A method in accordance with claim 1 in which the said monoamine is cyclohexylamine.

21. A method in accordance with claim 1 in which the said monoamine is butylmonoethanolamine.

22. Viscose in accordance with claim 7 in which the said monoamine is n-amylamine.

23. Viscose in accordance with claim 7 in which the said monoamine is cyclohexylamine.

24. Viscose in accordance with claim 7 in which the said monoamine is butylmonoethanolamine.

NORMAN LOUIS COX.

REFERENCES CITED

The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,535,044

December 26, 1950

NORMAN LOUIS COX

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, lines 68 and 69, for the word "butylmonolamine" read *butylmonoethanolamine*; column 6, line 67, for "A7-6" read *A 7-6*; column 7, line 15, for "collulose" read *cellulose*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of May, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.