

1

2,855,321

VISCOSE PROCESS

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This invention relates to the manufacture of regenerated cellulose structures by the viscose process. More particularly, it relates to improvements in the process of spinning monoamine-modified viscose solution for the production of regenerated cellulose articles.

It is known that when viscose is extruded into acid coagulating baths containing zinc salts in the presence of certain nitrogen-containing organic compounds, regenerated cellulose yarns of vastly improved physical properties are produced. The filaments which make up the yarn are characterized by unusual cross section and surface features. The filaments display no appreciable crenulations so that the surface is relatively smooth. The ratio of skin to core measured radially in a typical cross section is greater than one and in many cases the filament cross section may display only skin. (The greater the amount of skin, the greater is the improvement in properties.) Furthermore, the swelling of both the freshly spun gel yarn and the yarn after drying (the secondary swelling) is reduced. These characteristics, it has been found, correlate with the high tenacity and high fatigue resistance in yarns and cords produced from the filaments. The nitrogen-containing organic compounds suggested as modifiers for producing these exceptional yarns include certain classes of amines, quaternary ammonium compounds and dithiocarbamates. These compounds are described in U. S. Patents 2,535,044, 2,535,045 and 2,536,014 all issued to N. L. Cox on December 26, 1950, and 2,696,423 issued December 7, 1954, to M. A. Dietrich.

The amine-modified viscose spinning solutions described in U. S. Patent No. 2,535,044 are prepared by adding the amine to completely xanthated alkali cellulose. When added in this way, at least 1 millimol of amine per 100 grams of viscose is required for the modifier to be effective, and much larger amounts up to 10 millimols per 100 grams of viscose are usually required. The expense involved in using such large amounts of modifier increases the cost of the rayon appreciably; this is obviously undesirable for a commercial process.

The object of this invention is an improved process of preparing monoamine-modified viscose spinning solutions for manufacturing regenerated cellulose filaments, yarns and cords. Another object is a viscose spinning process in which much smaller amounts of monoamine modifier than had previously been found necessary will be effective for producing regenerated cellulose filaments having low gel swelling values, no appreciable crenulation and a skin-to-core ratio when measured radially of substantially greater than one. Other objects will appear hereinafter.

The objects are accomplished by adding to a specially-prepared viscose spinning solution a tertiary monoamine having a maximum of 8 carbon atoms in any one radical, having at least one radical with a hydroxyl group attached to a carbon atom and being soluble in a 6% aqueous sodium hydroxide solution to the extent of at least 0.1% by weight.

The special preparation of the viscose spinning solution comprises xanthating alkali cellulose with carbon di-

2

sulfide so that not more than 90% of the desired final xanthation occurs in the customary dry phase xanthation, mixing the partially xanthated alkali cellulose with dilute aqueous caustic solution to a cellulose content of 4% to 15% and treating the mixture with carbon disulfide to provide the desired final xanthation.

The tertiary monoamine is incorporated into the viscose spinning solution during the second xanthation step, either immediately prior to or within twenty minutes after the addition of carbon disulfide. The monoamine may be added with the caustic solution, with the carbon disulfide or separately. The amount added per 100 grams of the viscose spinning solution can be as little as 0.02 millimol and up to 1 millimol, preferably 0.1 to 0.85 millimol.

The viscose spinning solution, prepared in the above manner, is preferably heated to 40° C. to 80° C. prior to extrusion. It is extruded into an acid coagulating bath containing at least 2%, preferably 5% to 15%, of zinc sulfate.

The invention will be more clearly understood by referring to the examples and discussion which follow. Unless otherwise stated, all percentages in the examples, the discussion and the claims are by weight. Case A of Example I sets forth the best mode contemplated for carrying out the invention. It is compared to various modes of operation outside the scope of the invention. The other examples set forth specific embodiments of the process invented. The examples are not to be construed in any sense as limitative of the invention.

In the tables, the following symbols are used:

- T_d is dry tenacity in grams/denier
- T_w is wet tenacity in grams/denier
- T_l is loop tenacity in grams/denier
- E_{d, w, l} are percent elongations; dry, wet and loop
- T_c is conditioned tenacity in grams/denier
- T_{o. d.} is oven-dry tenacity in grams/denier
- E_{15 lbs.} is percent elongation when a load of 15 lbs. is applied
- D. B. Fatigue is the number of minutes required to break the cord with the "dynamically balanced" fatigue tester

The measurements are conventional with the possible exception of the D. B. Fatigue test. In the D. B. Fatigue test, a cord is conditioned for 48 hours at 24° C. and 54% relative humidity and clamped in jaws set 16.75 inches apart. A load of 1 gram/denier is applied and the cord is brought to 100° C. while in place in the machine for about one-half hour. The jaws are then oscillated to stretch the cord 3000 times per minute using a stroke of 0.24 inch. The number of minutes survived before breaking is recorded as the D. B. Fatigue.

EXAMPLE I

A viscose solution containing 6.25% cellulose and 5.75% total alkali, calculated as sodium hydroxide, and a tertiary monoamine was prepared from wood pulp sheets using a total of about 38% carbon disulfide, based on the air-dry weight of the pulp.

In cases A, B and C, 26.6% carbon disulfide, based on the air-dry weight of the pulp, was added in the baratte and 11.4% carbon disulfide was added in the mixer. Thus, 70% of the xanthation occurred in the baratte and 30% occurred in the mixer. In experiment D all the carbon disulfide was added to the alkali cellulose in the baratte.

In all cases, the amine modifier was added to the mixing caustic in the mixer prior to introducing the xanthated alkali cellulose from the baratte. 0.5 millimol of triethanolamine per 100 grams of viscose was used in case A; 0.65 millimol of triethylamine and N-methyl morpholine (tertiary amines with no hydroxyl groups at-

3

tached to a carbon atom and outside the scope of the invention) per 100 grams of viscose was used in cases B and C, respectively; and 1.0 millimol of triethanolamine per 100 grams of viscose was used in case D (where the xanthation process was outside the scope of the invention).

The viscose solutions were filtered, deaerated and permitted to ripen to a salt index of 17.5 and to attain a viscosity of about 30 stokes. Prior to spinning, the solutions were passed through a coil type heater immersed in a tank of hot water. The solutions were heated to a temperature of about 44° C. and then extruded into a bath maintained at about 60° C. containing about 9.3% sulfuric acid, about 17.5% sodium sulfate and about 9.5% zinc sulfate.

The filaments were first led through a trumpet-like tube in the bath and then, by means of tension rollers in the bath, were stretched 70% to 80%. After leaving the bath, the filaments passed over two feed wheels in succession, the feed wheels being sufficiently different in diameter to stretch the filaments an additional 20%. During this latter stretching the filaments were treated with diluted bath solution at about 90° C. The filaments were then led into a rotating bucket at a speed of 100 yards per minute to form cakes. The cakes were purified, slashed and processed into tire cord in the conventional manner.

The yarn and cord properties are compared in Table I below:

Table I

Case.....	A	B	C	D
Yarn Properties:				
Denier.....	1,727	1,631	1,624	1,613
T _d	4.42	4.57	4.19	4.21
T _w	3.04	2.93	2.77	2.74
T ₁	3.13	3.05	2.86	2.93
E _d	11.2	9.1	7.8	8.2
E _w	25.3	21.6	18.6	16.9
E ₁	6.6	5.3	4.8	5.3
Cord Properties:				
Denier.....	3,865	3,700	3,624	3,564
T _o	3.38	3.17	3.11	3.23
T _o d.....	3.87	3.66	3.37	3.75
E ₁₅ lbs.....	7.9	8.0	7.0	6.5
D. B. Fatigue.....	328	100	51	130
Filament Cross Section:				
Crenulated.....	no	yes	yes	yes
Percent skin, radially.....	100	less than 50	less than 50	60

EXAMPLE II

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight total alkali calculated as sodium hydroxide, and 0.6 millimol of diethylethanolamine per 100 grams of viscose was prepared from wood pulp sheets by a procedure identical to that described for case A in Example I.

The solution had a salt index of 17.3 and a viscosity of 29.5 stokes. It was heated to 44° C. and spun into a coagulating and regenerating bath at about 60° C. The composition of the bath and the ensuing treatments of filaments were those presented in Example I.

The following properties were obtained:

YARN PROPERTIES

Denier	T _d	T _w	T ₁	E _d	E _w	E ₁
1,653.....	4.46	3.13	3.09	9.3	21.3	5.7

CORD PROPERTIES

Denier	T _o	E ₁₅ lbs.	T _o d.	D. B. Fatigue
3,696.....	3.32	7.2	3.83	250

4

EXAMPLE III

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight of alkali calculated as sodium hydroxide, and 0.65 millimol of methyl-diethanolamine per 100 grams of viscose was prepared by the procedure described for case A in Example I.

The viscose solution at a salt index of 17.5 and a viscosity of 29.5 stokes was heated to 44° C. and extruded, treated and processed according to the details described in Example I.

The following properties were obtained:

YARN PROPERTIES

Denier	T _d	T _w	T ₁	E _d	E _w	E ₁
1,666.....	4.35	3.02	2.96	8.8	20.8	5.2

CORD PROPERTIES

Denier	T _o	E ₁₅ lbs.	T _o d.	D. B. Fatigue
3,690.....	3.32	6.1	3.76	245

EXAMPLE IV

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight of alkali calculated as sodium hydroxide, and 0.71 millimol of tri-isopropanolamine per 100 grams of viscose was prepared from sheets of wood pulp according to the process described for case A in Example I.

The solution was heated to 44° C. and spun into the coagulating bath of Example I. The subsequent processing of the filaments was essentially equivalent to that described in Example I.

The following properties were obtained:

YARN PROPERTIES

Denier	T _d	T _w	T ₁	E _d	E _w	E ₁
1,634.....	4.52	3.05	3.17	9.4	21.7	5.9

CORD PROPERTIES

Denier	T _o	E ₁₅ lbs.	T _o d.	D. B. Fatigue
3,697.....	3.36	7.5	3.83	273

EXAMPLE V

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight total alkali calculated as sodium hydroxide, and 0.1 millimol of tri-ethylethanolamine per 100 grams of viscose was prepared from wood pulp sheets by a procedure identical to that described for case A in Example I.

The solution had a salt index of 17.3 and a viscosity of 29.5 stokes. It was heated to 44° C. and spun into a coagulating and regenerating bath at about 60° C. The bath contained 7.5% sulfuric acid, 17.5% sodium sulfate, 9.5% zinc sulfate and 100 parts per million of nitrogen arising from modifier leached from the extruded filaments. The ensuing treatments of filaments were as presented in Example I.

The following properties were obtained:

YARN PROPERTIES

Denier	T _d	T _w	T ₁	E _d	E _w	E ₁
1,659.....	4.49	3.12	3.11	9.3	21.6	6.1

CORD PROPERTIES

Denier	T _c	E ₁₅ lbs.	T _{0. d.}	D. B. Fatigue
3,698.....	3.34	7.2	3.84	259

As shown in the foregoing examples, there are two critical elements involved in the practice of this invention: xanthating the alkali cellulose in two separate steps and using a special class of tertiary monoamines. Unless the amine contains at least one radical with a hydroxyl group attached to the amino nitrogen, splitting xanthation provides no significant improvement. (Note Example I cases A, B and C.) On the other hand, without splitting xanthation the use of tertiary monoamines of the class specified provides no significant property improvement. (Note Example I cases A and D.) The importance of the two limitations is illustrated most vividly by the difference in fatigue properties of the rayon cords.

In the process of the invention, the alkali cellulose is prepared in the conventional manner. Sheets of wood pulp or cotton linter cellulose are soaked in caustic alkali solution. Excess caustic solution is drained and pressed from the saturated sheets. The resulting alkali cellulose is shredded and aged to provide the desired viscosity in the viscose solution ultimately prepared. The shredded alkali cellulose is then dropped into a rotatable drum called a baratte for the first xanthation step.

The alkali cellulose is partially xanthated in the baratte by the addition of carbon disulfide. The amount of carbon disulfide added is such that not over 90% of the total xanthation contemplated occurs in the baratte.

The partially xanthated alkali cellulose is now added to a tank where it is mixed with a measured quantity of dilute aqueous caustic soda solution and the remaining carbon disulfide is added. Specifically, the partial xanthate is added to a conventional viscose mixer filled with the caustic solution to provide a cellulose content of 4% to 15%; is mixed for about 5 to 30 minutes to dissolve the partial xanthate; sufficient carbon disulfide is added to complete the xanthation; and, if necessary, the mixture is diluted with dilute caustic or water to give a cellulose content of 4% to 10% and a total alkali content, calculated as sodium hydroxide, of 4% to 8% in the final mixture. The amount of carbon disulfide added is such that at least 10% of the xanthation occurs in the mixing cycle. The amount of carbon disulfide used in both steps should total at least 30%, preferably 35% to 45%, based on the weight of the air-dried cellulose originally charged to the steeping press. For a detailed description of this process, attention is called to a copending application, U. S. Serial No. 351,592, filed April 28, 1953, now Patent No. 2,801,998, to A. Robertson.

About 0.02 to about 0.85 millimol per 100 grams of viscose of the special monoamine modifier is preferably added during the mixing cycle. The addition is made preferably prior to or within twenty minutes after the start of the final xanthation step. The amine may be added with the caustic solution or with the carbon disulfide used for final xanthation or it may be added separately to the mixer.

Suitable tertiary monoamines are those that are soluble to the extent of 0.1% in 6% aqueous sodium hydroxide, have no radical containing more than 8 carbon atoms and have at least one radical with a hydroxyl group attached to a carbon atom. Radicals of more than 8 carbon atoms tend to decrease the solubility of the amine and produce surface activity which is undesirable in the process of the invention. Preferred tertiary monoamines, in addition to those illustrated in the examples, include ethyldiethanolamine, amyldiethanolamine, hexyldiethanolamine, cyclohexyldiethanolamine, butylmethylethanolamine and 4-morpholine-ethanolamine.

The amount of the tertiary monoamine required depends on several factors. In general, no more than about 0.85 millimol per 100 grams of viscose is necessary to obtain effective results. Under the most favorable conditions, as little as .02 millimol may be adequate. The optimum amount is lowered for the amines of higher molecular weight, by an increase in the total carbon disulfide used for xanthation and by increasing the level of amine concentration in the spinning bath. For best results, the amine concentration in the bath, measured as nitrogen, should not exceed 200 parts per million. However, the process of this invention is also operable with no amine in the bath, although this condition is difficult to maintain under ordinary spinning procedures.

The resulting viscose solution is filtered, deaerated and ripened to a salt index of at least 5 at a temperature of about 18° C. While the process of this invention yields improvements with ripe viscoses, it is preferable to restrict ripening and spin the viscose in an unripened or partially ripened state (at a salt index above 10).

Prior to spinning, the viscose solution is preferably heated. 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 viscose solution, preferably heated to a temperature of 40° C. to 80° C., is extruded through a spinneret into a coagulating and regenerating bath maintained at a temperature from 40° C. to 80° C. and containing 4% to 12% sulfuric acid, 5% to 25% sodium sulfate and 2% 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 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 feed wheels. The secondary bath may consist simply of water or of dilute (1% to 4%) sulfuric acid, or it may be a diluted coagulating bath at a temperature between 50° C. and 100° C. Total stretches of 70% to 105% are preferred for producing high tenacity yarns and as low as 30% may be acceptable for textile type yarns. From the last feed wheel, the yarn is fed into a rotating bucket to form a cake. The yarn is then washed and slashed. The slashing operation is well known and consists of stretching the yarn and applying a lubricating solution. The process described is the so-called bucket process. However, the bobbin process or any of the so-called continuous processes may also be used with similar results.

The process offers the advantages of simplicity and economy. The restrictions, although critical to the invention, do not require any substantial alteration of the conventional viscose process. The process employs relatively small, economical amounts of the amine modifiers with outstanding results. Splitting xanthation also provides several inherent advantages. The xanthation cycle is reduced resulting in greater productivity per baratte. Since less carbon disulfide is used in the baratte, the barattes are easier to clean and to ventilate.

The improved yarns obtainable through the process of this invention can be used instead of regular regenerated cellulose yarns for any purpose where the latter find application, more particularly in the textile and tire cord industries. Textile fabrics made from these yarns, either

7

continuous filament or staple, have high strength; resist soiling and abrasion; and are easily laundered. Fabrics for automobile and truck tires utilize the high tenacity and the high fatigue resistance of the yarns and cords to prolong the lives of the tires. These fabrics are also useful for reinforcing other rubber goods such as commercial V-belts and the like.

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

Having fully disclosed the invention, I claim:

1. The process for preparing a monoamine-modified viscose spinning solution which comprises the steps of partially xanthating alkali cellulose with carbon disulfide in a dry phase so that up to 90% of the total xanthation contemplated occurs; mixing the partially xanthated alkali cellulose with aqueous sodium hydroxide solution to a cellulose content of 4% to 10% and a caustic content of 4% and 8%; adding carbon disulfide and a tertiary monoamine modifier, said modifier having a maximum of eight carbon atoms in any one radical, having at least one aliphatic radical with a hydroxyl group attached to a carbon atom, and being soluble to the extent of at least 0.1% in 6% caustic soda solution; and completing the xanthation to form a viscose solution having a content of 0.02 to 1 millimol of monoamine per 100 grams of viscose.

2. A process as defined in claim 1 in which the tertiary monoamine modifier is added to the partially xanthated alkali cellulose prior to the start of the final xanthation step.

3. A process as defined in claim 1 in which the amount of tertiary monoamine added is from 0.1 to 0.85 millimol of modifier per 100 grams of viscose.

4. A process as defined in claim 1 in which the tertiary monoamine is N-methyldiethanolamine.

5. A process as defined in claim 1 in which the tertiary monoamine is diethylethanolamine.

6. A process as defined in claim 1 in which the tertiary monoamine is triethanolamine.

7. A process as defined in claim 1 in which the tertiary monoamine is tri-isopropanolamine.

8. A process for preparing a viscose spinning solution which comprises the steps of partially xanthating alkali cellulose with carbon disulfide in a dry phase so that up to 90% of the total xanthation contemplated occurs; mixing the partially xanthated alkali cellulose with aqueous caustic solution to a cellulose content of 4% to 15%; completing xanthation by adding carbon disulfide in the

8

presence of 0.02 to 1 millimol per 100 grams of viscose spinning solution of a tertiary monoamine having a maximum of 8 carbon atoms in any radical, at least one radical being aliphatic with a hydroxyl group attached to a carbon atom and being soluble in a 6% aqueous sodium hydroxide solution to the extent of at least 0.1% by weight; and diluting the xanthated alkali cellulose to a cellulose content of 4% to 10% and a caustic content of 4% to 8%.

9. In the process of spinning modified viscose to provide improved rayon yarns and cords, the steps of partially xanthating alkali cellulose with carbon disulfide in a dry phase so that up to 90% of the total xanthation occurs; mixing the partially xanthated alkali cellulose with aqueous caustic solution to a cellulose content of 4% to 15%; completing the xanthation with carbon disulfide in the presence of 0.02 to 1 millimol of a tertiary monoamine modifier per 100 grams of final viscose solution, said modifier having a maximum of 8 carbon atoms in any one radical, having at least one aliphatic radical with a hydroxyl group attached to a carbon atom and being soluble to the extent of at least 0.1% in 6% caustic soda solution; diluting the xanthated mixture to form a viscose solution containing 4% to 10% of cellulose and 4% to 8% of caustic; heating said viscose solution; and extruding said viscose solution into a spinning bath containing 4% to 12% sulfuric acid, 5% to 25% sodium sulfate, and 2% to 15% zinc sulfate.

10. A process as defined in claim 9 in which the tertiary monoamine modifier is added to the partially xanthated alkali cellulose prior to the start of the final xanthation step.

11. A process as defined in claim 9 in which the amount of tertiary monoamine modifier added is from 0.1 to 0.85 millimol of modifier per 100 grams of viscose.

12. A process as defined in claim 9 in which both the spinning bath and the viscose spinning solution are at 40° C. to 80° C. prior to spinning.

13. A process as defined in claim 9 in which the amount of zinc sulfate in the spinning bath is 5% to 15%.

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