

2,810,658

PROCESS FOR SPINNING MODIFIED VISCOSE SOLUTION

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This invention relates to the production of artificial filaments, yarns and cords of regenerated cellulose by the viscose process. More particularly, the invention is concerned with improvements in the process of spinning monoamine-modified viscose in the production of rayon.

It has recently been discovered that marked improvements in rayon filaments are obtained by adding monoamine modifiers to the viscose spinning solution or to the spinning bath. The modified filaments obtained by spinning modified viscose solution under suitable conditions, as disclosed in U. S. Patent No. 2,535,044, issued December 26, 1950, to Norman Louis Cox or spinning unmodified viscose into modified baths as disclosed in U. S. Patent No. 2,535,045; are readily distinguished from unmodified rayon filaments by their smooth surfaces, i. e., the surfaces display no appreciable crenulation whereas the ordinary filaments are highly crenulated. When dyed cross-sections are examined under a microscope, the modified filaments are characterized by having considerably more skin than core, whereas normal rayon is mostly core with only a very thin skin. Yarn composed of these modified filaments is denser than that from otherwise comparable unmodified filaments, dyes more rapidly and, even more important, has markedly improved tenacity, fatigue resistance and abrasion resistance. Representative yarn and cord properties for filaments spun from unmodified and modified viscose under otherwise comparable conditions are as follows:

	Yarn Properties					Cord Properties		
	Denier	T _D	T _W	T _L	E _D	T _C	T _{OD}	D. B. Fatigue
Unmodified.....	1656	3.8	2.2	2.8	9.7	2.8	3.2	75
Modified.....	1662	4.4	3.0	3.1	9.6	3.3	3.6	240

where

- T_D is dry tenacity in grams per denier,
- T_W is wet tenacity in grams per denier,
- T_L is loop tenacity in grams per denier,
- E_D is percent dry elongation,
- T_C is conditioned tenacity in grams per denier
- T_{OD} is oven-dry tenacity in grams per denier and
- D. B. fatigue is the number of minutes required to break the cord with the "dynamically balanced" fatigue tester.

These tests are conventional with the possible exception of the D. B. fatigue test. In this 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 per 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 3,000 times per minute using a stroke of 0.24 inch.

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

It is an object of this invention to provide a process for preparing modified viscose spinning solution so that much smaller amounts of monoamine modifier than have previously been found necessary will be effective for producing rayon having the improved properties described above. Another object is to improve the process of spinning monoamine-modified viscose spinning solution to provide rayon yarns and cords which exhibit a still further marked improvement in properties. Other objects of this invention will become apparent from the following description and claims:

These objects are accomplished by splitting the xanthation of alkali cellulose, so that not more than 90% of the desired final xanthation is accomplished by the customary dry phase xanthation with carbon disulfide, and then incorporating the monoamine modifier during a final stage of xanthation in which the partial xanthate is mixed with dilute aqueous caustic solution to a cellulose content of 4% to 15% and treated with carbon disulfide to complete the xanthation. When the viscose solution is prepared in this way a surprising reduction in the amount of monoamine can be made. The amount added per 100 grams of the final viscose solution can be as little as about 0.02 millimole, or less, and not more than about 1 millimole for any of the monoamines encompassed by this invention. For best results from 0.1 to 0.85 millimole per 100 grams of viscose is preferred. A further unexpected result of this process is that even better properties are obtained in the spun rayon.

The alkali cellulose used is prepared in the conventional manner, which involves soaking sheets of wood pulp or cotton linter cellulose in caustic alkali solution, draining the caustic solution from the saturated sheets, pressing excess caustic from the sheets, shredding the resulting alkali cellulose and aging the alkali cellulose to provide the desired viscosity in the viscose ultimately prepared. The alkali cellulose is placed in a rotating drum called a baratte. Carbon disulfide is added and the baratte is rotated to provide mixing. Xanthation of the alkali cellulose occurs and is continued until an absolute xanthate sulfur substitution value of at least 13% is obtained, based on the cellulose content of the material. However, only a partial xanthate sulfur substitution is to be achieved in this step, as the xanthation must be completed under different conditions in the presence of the modifier. Based on the absolute xanthate sulfur substitution value obtained in the final xanthation, the xanthation is split so that not over 90% of the xanthate sulfur substitution occurs in this first step, e. g., if a final absolute value of 27.0% is desired, the absolute xanthate sulfur substitution value at the conclusion of this first step must not exceed 24.3%. In order to avoid confusion, the proportion of the total xanthation accomplished in this first step will be referred to as the relative xanthate sulfur substitution value.

Preferably the relative xanthate sulfur substitution value should be less than 85%.

The partially xanthated material is now mixed with a measured quantity of dilute aqueous caustic soda solu-

tion sufficient to give a cellulose content of 4% to 15% and a cellulose: caustic ratio approximating that of the final viscose solution. Preferably the partial xanthate is added to a conventional viscose mixer filled with the caustic solution in proportions giving a cellulose content of 4% to 10% and a caustic content of 4% to 8% in the final mixture, mixed for about 5 to 30 minutes to dissolve the partial xanthate, and sufficient carbon disulfide is added to complete the xanthation. Other methods of accomplishing this part of the xanthation are disclosed in copending U. S. application Serial No. 351,592 of Andrew Robertson, which is assigned to the assignee of the present application.

The monoamine modifier should be incorporated into the viscose during the final stage of xanthation. For this purpose the addition of the modifier is preferably prior to or within twenty minutes after the start of the final xanthation reaction. The modifier may be added with the caustic solution or with carbon disulfide for the final xanthation step, or may be added separately to the mixture. Suitable modifiers are organic primary or secondary monoamines, i. e., having at least one hydrogen atom attached to the amino nitrogen, said amine having at least two and preferably at least four carbon atoms, but containing no more than eight carbon atoms in any one radical, and should be soluble to the extent of at least 0.1% in 6% caustic soda solution. Illustrative of these modifiers are cyclohexylamine, N-methylcyclohexylamine, N-ethylcyclohexylamine, diethylamine, morpholine and ortho-methyl-N-methylcyclohexylamine.

The resulting viscose solution is filtered, deaerated and may be permitted to ripen at a temperature of about 18° C. The viscose is then pumped to the spinning machine. The yarn fatigue resistance may be improved by heating the viscose, as by means of a small oil-bath heat exchanger placed between the spinning pump and the spinneret. Heating may be accomplished with any suitable heating medium, such as steam, hot water, oil, or coagulating bath; or an electric heating unit may be inserted in the pipe.

The viscose spinning solution, which may be heated before spinning, preferably to 40°–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, 13 to 25% sodium sulfate and 2 to 15% zinc sulfate. The zinc sulfate is an essential component of the spinning bath. 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. A spinning tube may be used as described in Millhiser U. S. Patent No. 2,440,057 to confine the filaments in their critical stage of formation so that no substantial tension is imposed upon them. When spinning the monoamine-modified viscose of this invention, the concentration in the spinning bath of modifier or reaction products with the modifier will inevitably build up. Since it is difficult to determine the form of the modifier in the bath, this concentration is simply expressed in terms of parts per million of nitrogen. In order to obtain the results of my invention, it is important to maintain this level of modifier in the bath below about 200 parts per million of nitrogen by extracting any excess during recirculation of the spinning bath. The bath may contain no nitrogen but in commercial practice it is more likely to contain between 20 and 200 parts per million. It has been found that the larger the concentration of nitrogen

in the bath, the smaller the concentration of modifier required in the viscose.

After extrusion, the filaments are given a travel of 100–250 inches in the primary bath by means of a multiple roller set-up which gradually applies tension to the traveling filaments and thereby orients them while they are still plastic. The preferred method is to apply a part of the stretch beyond the primary bath in a secondary bath or between feed wheels. The secondary bath may consist simply of water or of dilute (1–4%) sulfuric acid, or it may be diluted coagulating bath. The temperature of the secondary bath is preferably between 50° C. and 100° C. Total stretches of 80–105% are preferred for producing high tenacity yarns and 30–105% 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 be used with similar results.

The invention will be more clearly understood by referring to the examples below of preferred embodiments of the invention, and the discussion which follows. In the tables of these examples the meaning of the symbols is as previously defined.

Example I

Alkali cellulose, prepared from sheets of wood pulp in the conventional manner, was placed in a baratte. Thirty-two percent carbon disulfide (based on the weight of air-dried pulp) was added in the baratte to achieve a xanthate substitution (percent xanthate sulfur based on the cellulose present) of 21.7. The partially xanthated alkali cellulose was then fed into a mixer which contained dilute caustic solution and also contained cyclohexylamine. Twenty-five minutes later, 7% carbon disulfide (based on the weight of air-dried pulp) was added to produce a total xanthate substitution of 27.1. Thus 80% of the total xanthate substitution was accomplished during the first xanthation step and the cyclohexylamine modifier was added prior to the second xanthation step. The proportions were controlled to give a viscose solution containing 6.25% by weight of cellulose, 5.75% sodium hydroxide and 0.049% cyclohexylamine (0.49 millimoles of cyclohexylamine per 100 grams of viscose).

The viscose solution was filtered, deaerated and permitted to ripen to a salt index of 17.5 and to attain a viscosity of 29.5 stokes. Prior to spinning, the solution was passed through a coil-type heater immersed in a tank of hot water. The solution was heated to a temperature of about 44° C. and then extruded into a bath maintained at 60.5° C. containing 9.3% sulfuric acid, 17.5% sodium sulfate, and 9.5% zinc sulfate. The nitrogen content of the bath was maintained at 40–50 p. p. m. by removing excess during recirculation of the bath.

The filaments were first led through a trumpet-like tube in the bath and then, by means of tension rollers in the bath, they were stretched 70–80%. After leaving the bath the filaments passed over two feed wheels in succession having a differential in speed to stretch the filaments an additional 20%. During this latter stretching, the filaments were treated with diluted bath solution. The filaments were then led into a revolving bucket to form cakes. The cakes were purified, slashed and processed into tire cord in the conventional manner.

The following properties were obtained:

Yarn Properties							Cord Properties				
Denier	T _D	T _W	T _L	E _D	E _W	E _L	Denier	T _C	E _{18 lbs.}	T _{OD}	D. B. Fatigue
1643	4.57	3.16	3.21	9.0	24.8	5.3	3690	3.43	7.4	3.79	463

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The example was re-run except that the viscose spinning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

Example II

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight sodium hydroxide and 0.07% by weight cyclohexylamine (0.7 millimole per 100 grams of viscose) was prepared from wood pulp sheets by a procedure identical to that described in Example I except for the amount of cyclohexylamine.

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 coagulating and regenerating bath at 60.5° 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							Cord Properties				
Denier	T _D	T _W	T _L	E _D	E _W	E _L	Denier	T _C	E _{15 lbs.}	T _{OD}	D. B. Fatigue
1638	4.41	3.17	3.27	9.1	25.2	6.0	3650	3.42	7.4	3.76	394

The example was re-run except that the viscose spin-

The following properties were obtained:

Yarn Properties					Cord Properties				
Denier	T _D	T _W	T _L	E _D	Denier	T _C	E _{15 lbs.}	T _{OD}	D. B. Fatigue
1699	4.32	3.13	3.32	10.7	3786	3.45	7.5	3.94	440

ning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

Example III

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight sodium hydroxide and 0.049% by weight cyclohexylamine (0.49 millimole per 100 grams of viscose) was prepared by the split xanthation process of Example I. However, in this example 28% carbon disulfide (based on the weight of air-dried pulp) was added in the baratte to achieve a xanthate

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The example was re-run except that the viscose spinning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

Example V

Example I was repeated with 0.024% N-methylcyclohexylamine in the viscose, instead of the 0.049% cyclohexylamine, and with the addition of sufficient N-methylcyclohexylamine to the spinning bath to maintain a concentration of about 0.056%, corresponding to 70 p. p. m. based on the nitrogen content of the bath.

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The following properties were obtained:

Yarn Properties					Cord Properties				
Denier	T _D	T _W	T _L	E _D	Denier	T _C	E _{15 lbs.}	T _{OD}	D. B. Fatigue
1681	4.30	3.10	3.22	11.3%	3739	3.48	7.8	3.91	475

substitution of 19.0%, based on the cellulose present, and an additional 11% CS₂ was added in the mixer to achieve a final xanthate substitution of 27.1. Hence 70% of the total xanthate substitution occurred in the baratte instead of 80% as in the previous examples.

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							Cord Properties				
Denier	T _D	T _W	T _L	E _D	E _W	E _L	Denier	T _C	E _{15 lbs.}	T _{OD}	D. B. Fatigue
1645	4.50	3.10	3.26	9.6	25.5	5.6	3682	3.43	7.5	3.72	372

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The example was re-run except that the viscose spinning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

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Example IV

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight sodium hydroxide and 0.024% N-methylcyclohexylamine (0.21 millimole per 100 grams of viscose) was prepared from sheets of wood pulp according to the split xanthation process described 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.

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according to the split xanthation process described in Example I. The solution was heated to 44° C. and extruded into a bath at 63° C. containing 9.1% sulfuric acid, 17.5% sodium sulfate, 9.5% zinc sulfate and .008% N-methylcyclohexylamine.

The filaments were stretched 110% and collected on a bobbin. They were processed in accordance with the conventional bobbin process. The following properties were obtained:

Yarn Properties					Cord Properties				
Denier	T _D	T _W	T _L	E _D	Denier	T _C	E ₁₅ lbs.	T _{OD}	D. B. Fatigue
1691	4.24	2.94	3.18	10.5	3740	3.48	7.8	3.82	507

The example was re-run except that the viscose spinning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

Example VII

Morpholine and diethylamine, representative of commercially accessible secondary amines, were also tested on a smaller scale (so-called blow case spinning). A vis-

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was prepared from wood pulp sheets according to the split xanthation process. Eighty percent of the xanthation occurred in the baratte and 20% in the mixer with a total of 41% carbon disulfide (based on the air-dried pulp) used.

In this case, the cyclohexylamine was added after the carbon disulfide for the second xanthation step had been added. The partially xanthated alkali cellulose was fed into the mixer which contained dilute caustic solution.

Twenty-five minutes later, 7.4% carbon disulfide was added. Ten minutes after this addition of carbon disulfide, the cyclohexylamine was added.

The solution was then filtered, deaerated and permitted to ripen slightly. Prior to spinning, the solution was heated to 44° C. and extruded, processed, etc., in the manner described in Example I.

The following properties were obtained: The yarn, in cross-section, exhibited 85-90% skin, based on radial measurement.

Yarn Properties					Cord Properties					
Denier	T _D	T _W	T _L	E _D	Denier	T _C	E ₁₅ lbs.	T _{OD}	Percent Conv.	D. B. Fatigue
1654	4.55	3.18	3.32	9.2%	3679	3.52	6.9%	3.80	77.3%	310

cose spinning solution containing 6.25% by weight cellulose, 5.75% by weight sodium hydroxide was prepared by the split xanthation process, as described in Example I, using 37% carbon disulfide. Eighty percent of the total xanthate sulfur substitution was permitted to occur in the first xanthation step. In one case, 0.05% by weight of morpholine (0.57 millimole per 100 g. viscose) was used. In the second case, the viscose spinning solution contained .048% by weight of diethylamine (0.66 millimole per 100 g. viscose). The spinning bath compositions and processing followed, in general, the operations described in Example I except that no nitrogen built up in the spinning bath.

A filament having a smooth cross-section and composed of from 95 to 100% skin was obtained in both cases. The following physical properties were also obtained:

Yarn Properties					Cord Properties				
Denier	T _D	T _W	T _L	E _D	Denier	T _C	E ₁₅ lbs.	T _{OD}	D. B. Fatigue
Morpholine									
1620	4.74	3.02	3.31	9.8%	3593	3.52	7.4%	3.83	234
Diethylamine									
1591	4.71	3.05	3.18	9.0%	3550	3.49	7.1%	3.88	223

The example was re-run except that the viscose spinning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

Example VIII

A viscose spinning solution containing 6.25% by weight cellulose, 5.75% by weight sodium hydroxide and .056% cyclohexylamine (0.56 millimole per 100 grams viscose)

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The example was re-run except that the viscose spinning solution was not passed through a heater prior to spinning. Similar results were obtained as indicated by a product displaying in cross-section greater than 85% skin measured radially.

The following monoamines were substituted for cyclohexylamine in the processes described in Example I:

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|----------------------------|--|
| 9. n-Amylamine | 14. Pyridine |
| 10. N-butylethanolamine | 15. Piperidine |
| 11. Diethanolamine | 16. Ortho-methyl, N-methyl-cyclohexylamine |
| 12. Ethylethanolamine | 17. Ortho-methyl, N-ethylcyclohexylamine |
| 13. N-ethylcyclohexylamine | |

50 In all cases, the filaments produced had cross-sections which displayed more than 75% skin measured radially.

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Since this quantity of skin had produced the excellent properties in the yarns and cords of this invention, this was considered to be sufficient evidence that the above monoamines could be used with similar results in the process of my invention.

75 Preferred primary and secondary monoamine modifiers for the purpose of this invention are those in which the amino nitrogen is attached to hydrocarbon groups, preferably alkyl groups, and/or hydroxy alkyl groups. Suitable modifying agents in addition to those illustrated in the ex-

amples include butylamine, hexanolamine, dipropylamine, dipropanolamine, N-ethylethanamine, N-propylethanamine, N-amylethanamine, N-hexylethanamine, N-cyclohexylethanamine, N-propylpropanamine, N-ethylcyclohexylamine or derivatives, such as ortho-methyl-N-methylcyclohexylamine and ortho-methyl-N-ethylcyclohexylamine. These contain at least 4 carbon atoms and have no radical of more than 8 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.

For effective results and for the most economic operation, very small quantities of amine modifiers are used. It is undesirable to use more than 1 millimole of agent per 100 grams of viscose; the generally preferred range being from 0.1 to 0.85 millimole per 100 grams of viscose. The optimum concentration of any given agent depends on its particular effectiveness and on its molecular weight. For example, smaller concentrations of N-methylcyclohexylamine will be as effective as larger concentrations of cyclohexylamine. The optimum concentration of modifier in the viscose also depends to some extent on process variables such as the spinning speed and the level of modifier concentration maintained in the bath. At the high spinning speeds used in industrial practice, less agent is desirable than at lower speeds. The amount of agent in the viscose should also be less with higher concentrations in the bath, but the nitrogen content of the bath should not exceed 200 p. p. m.

In practicing this invention, the viscose spinning solutions are prepared by the split xanthation process. The viscose solutions can contain from 4 to 15% cellulose and 4 to 8% alkali, preferably 5 to 7% cellulose and 4 to 6.5% alkali. The sum of carbon disulfide used in the two xanthation steps can be from 25 to 60% (based on the air-dried pulp).

The split xanthation process, besides being essential in the process of this invention, provides several inherent advantages. Split xanthation results in a shorter xanthation cycle. A reduced xanthation cycle results in greater productivity for the baratte. Furthermore, since less carbon disulfide is used in the baratte, cleaning the baratte, which had been time consuming and difficult, can be performed relatively quickly and easily. Splitting xanthation also provides more efficient reaction with carbon disulfide and a reduction in the problem involved in ventilating to remove poisonous carbon disulfide.

This invention permits the use of viscose displaying salt indices above 5, preferably above 10. The use of higher salt indices means a corresponding decrease in ripening time. Partially ripened and, in some cases, unripened viscoses may be spun by this process. Thus, economies are effected by shortening the viscose preparation cycle and by reducing the space required for this operation.

The high tenacity yarns and cords of this invention display outstanding fatigue resistance which is so important in the reinforcement of rubber goods, such as automobile tires, belts used in commercial operation and

the like. The abrasion characteristics and durability of the yarns can be advantageously utilized in preparing textile fabrics of exceptionally high launderability. These easily launderable fabrics can be prepared from yarns composed of either continuous filaments or staple fibers.

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

What is claimed is:

1. A process for spinning modified viscose to provide improved rayon yarns and cords comprising the steps of partially xanthating alkali cellulose with carbon disulfide in a dry phase in the absence of a monoamine modifier to an absolute sulfur substitution value of at least 13%, based on the cellulose content, and a relative xanthate sulfur substitution value of up to 90%, based on the absolute value obtained in the final xanthation; mixing the partially xanthated alkali cellulose with aqueous caustic solution to a cellulose content of 4% to 15% and a cellulose to caustic ratio approximating that of the final viscose solution; completing the xanthation with carbon disulfide in the presence of at least about 0.02 but less than 1 millimole of an organic monoamine modifier per 100 grams of final viscose solution, said organic monoamine modifier having at least one hydrogen atom attached to the amino nitrogen, containing at least four carbon atoms, having a maximum of eight carbon atoms in any one radical, and being soluble to the extent of at least 0.1% in 6% caustic soda solution; preparing a viscose solution containing 4% to 10% of cellulose and 4% to 8% of caustic from the modified cellulose xanthate mixture; and spinning the modified viscose solution into a spinning bath containing 4% to 12% sulfuric acid, about 13% to 25% sodium sulfate, 2% to 15% zinc sulfate and less than 200 parts per million of combined nitrogen at 40°-80° C.

2. A process as defined in claim 1 in which the organic monoamine modifier is selected from the group consisting of cyclohexylamine, N-methylcyclohexylamine, N-ethylcyclohexylamine, diethylamine, morpholine, n-ethylamine, N-butylethanamine, diethanolamine, ethylethanamine, pyridine, piperidine, ortho-methyl-N-methylcyclohexylamine, and ortho-methyl-N-ethylcyclohexylamine.

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

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