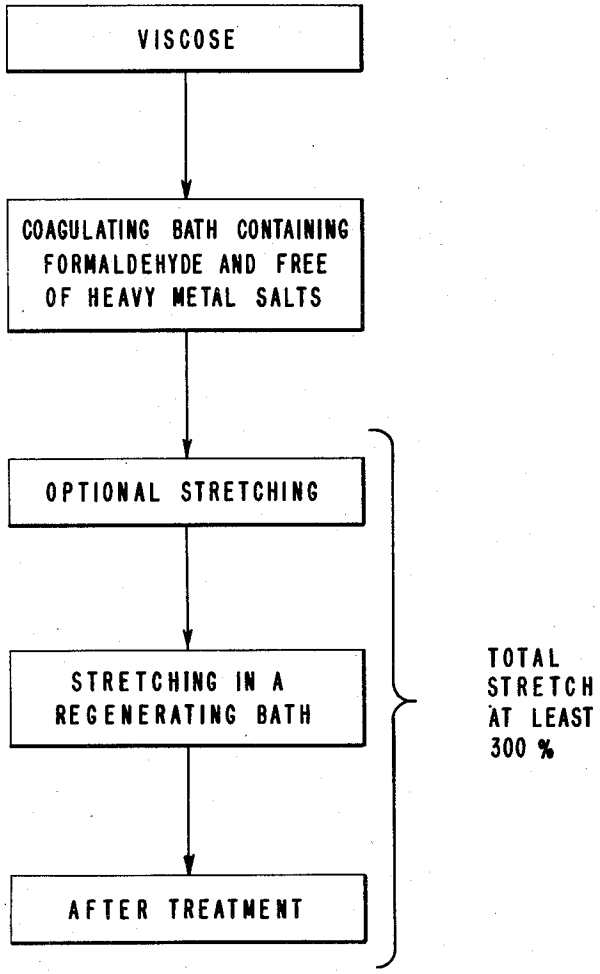
May 17, 1960 N. L. COX 2,937,070

VISCOSE PROCESS

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Fig. 1



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VISCOSE PROCESS

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This invention relates to the manufacture of regenerated cellulose structures from viscose spinning solutions. More particularly it relates to a process for improving the physical properties of regenerated cellulose filaments, especially the tenacity of fine denier filaments.

It is known (U.S. Patent No. 2,452,130) that when viscose is spun into a coagulating and regenerating bath containing conventional amounts of sulfuric acid, sodium sulfate and heavy metal sulfates such as zinc sulfate, the stretchability of the gel filament can be increased considerably by adding a small amount of formaldehyde to the spin bath. As disclosed in the above patent, the gel filaments can be stretched up to a limit of 140% in a secondary bath with a corresponding increase in tenacity to slightly over 4 grams/denier. As shown in the examples of the patent, the process was applied specifically to filaments of 2.5 denier/filament (100 denier/40 filaments).

An object of the present invention is to provide further improvements in stretchability, tenacity, dry and wet modulus. Another object is to provide a process particularly applicable to fine denier yarns, i.e., yarns composed of filaments up to 1.5 denier/filament. Such yarns are useful for preparing sheer textile fabrics, as reinforcement for thermosetting resins, etc. Other objects will appear hereinafter.

The objects are accomplished by a process which comprises extruding a highly xanthated (at least 23% xanthate sulfur based on cellulose content) viscose spinning solution through a plurality of orifices into an aqueous coagulating but non-regenerating bath free of heavy metal salts and containing by weight about 0.2% to 1.0% (preferably 0.3% to 0.8%) formaldehyde, from 2% to 11% (preferably 3% to 6%) sulfuric acid and 0 to 12% (preferably 8% to 12%) sodium sulfate, the sum of sulfuric acid and sodium sulfate concentrations being from 8% to 16%, to form filaments, and stretching the coagulated filaments to the maximum extent (300% to 450%) while passing them through at least one aqueous regenerating bath (preferably containing 1% to 4% sulfuric acid).

In a specific embodiment, there is added to the viscose solution prior to extrusion 0.5% to 2% based on the weight of viscose of an "alkali-soluble coagulation modifier" selected from the group consisting of ethers of the formula $RO—(CH_2CH_2O)_n—R'$, where R is alkyl or aryl, n is an integer from 1 to 4 and R' is hydrogen, alkyl or aryl and polyethylene oxides of molecular weight between 200 and 2,000. By the term "alkali-soluble coagulation modifier" is meant a modifier that is soluble in 6% aqueous sodium hydroxide to the extent of at least 1%.

It should be emphasized that no substantial stretch occurs in the coagulating bath; that the coagulating bath has substantially no regenerating action, i.e., that it decomposes less than 30% of the xanthate groups originally present in the viscose by the time the gel filament enters the secondary bath; that the coagulating bath must

not contain any heavy metal salts such as zinc sulfate; and that the stretch is applied after the filaments leave the coagulating bath in at least one regenerating bath or partly in air and partly in at least one regenerating bath.

By adhering to the process steps set forth above, stretches of 300% to 450% (amounts unheard of in prior processes) can be applied. The resulting filaments display smooth surfaces substantially free of crenulations or indentations and uniform, undifferentiated, circular or slightly elliptical cross-sections. The yarns are extremely strong, displaying tenacities of 5.5 grams/denier to as high as 8 grams/denier. Optimum results are obtained in the production of yarns having filament deniers less than 1.5, particularly 0.3 to 0.6 denier/filament. At these deniers, elongation and other important physical properties of the yarns are maintained at the most satisfactory level. Figure 1 is a schematic diagram of the process of the present invention.

The invention will be more clearly understood by referring to the examples and discussion which follow. Unless otherwise stated, all percentages in the specification and claims are by weight. Example 3 sets forth the best mode contemplated for carrying out 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:

$T_{d,w,l}$ are tenacities in grams/denier; dry, wet and loop
$E_{d,w,l}$ are percent elongations; dry, wet and loop
G.S. is the gel swelling factor

The measurements are conventional with the possible exception of the gel swelling measurement. Gel swelling was determined according to the following procedure. The yarn, composed of the coagulated filaments, was collected on a feed wheel or Godet wheel over a period of two minutes after leaving the coagulating bath. The sample was then wrapped in cheese cloth; centrifuged (3600 r.p.m.) for two minutes in a basket centrifuge; and weighed in a closed bottle. The sample was then treated with acid to regenerate cellulose; washed free of acid; dried in an oven at 105° C.; and weighed again. The ratio of the first weight (the gel weight) to the second weight (the cellulose weight) is the gel swelling.

Xanthate sulfur content, another term used in the examples and which is a measure of the degree of xanthation, was determined as follows. A 10 gram sample of viscose was dissolved in water and neutralized to a pH of 6.8 by the addition of sodium phosphate. Nitrogen was then bubbled through the viscose solution to drive off hydrogen sulfide and carbon disulfide resulting from the decomposition of sodium trithiocarbonate and other by-products. The resulting solution of cellulose xanthate was then acidified with 5 to 10 cc. of phosphoric acid; boiled for ½ hour while bubbling nitrogen through the solution to drive off carbon disulfide resulting from the decomposition of cellulose xanthate. The carbon disulfide was collected in a methanol-potassium hydroxide mixture, then oxidized with iodine solution. The quantity of iodine solution necessary to completely oxidize the carbon disulfide is a measure of the xanthate sulfur content of the viscose solution.

EXAMPLE I

A viscose solution containing 5% cellulose having a degree of polymerization (D.P.) of 525, 6% sodium hydroxide, and 1% of tetraethylene glycol dimethyl ether was prepared in the following manner. Alkali cellulose was first prepared from cotton linters and aged to get the desired viscose viscosity (30 to 60 poises). Then, the alkali cellulose was xanthated for 4.5 hours at 25° C.

using 62% carbon disulfide, based on the weight of bone-dry cellulose. The resulting xanthate crumbs were dissolved in aqueous sodium hydroxide. After mixing for 1.5 hours at a temperature below 15° C., tetraethylene glycol dimethyl ether was added and mixing was continued for 10 minutes. The freshly prepared viscose was filtered cold and kept at 0° C. until it was spun.

The viscose solution was spun in a relatively unripened state, with a high xanthate sulfur content (39.5% xanthate sulfur based on cellulose in the viscose) and with a low sodium trithiocarbonate content. It was spun into 270 denier, 240 filament yarn, i.e., a filament denier of 1.12, by extrusion through a spinneret having orifices of 0.0025" diameter into a primary coagulating bath at 50° C. The primary bath contained 10% sulfuric acid, 0.8% formaldehyde and no sodium sulfate. The yarn was given a primary bath travel of approximately 30 inches by using a roller guide. No substantial tension was imposed on the yarn since the feed wheel speed did not exceed the jet velocity. After leaving the coagulating bath where no stretch occurred, the yarn was given 133% stretch in air and then stretched in a bath containing 1% sulfuric acid at 95° C. to a total of 390%. The yarn was collected at a windup speed of 28 yards/minute. The spinning apparatus and collection device were essentially the same as those used commercially in the so-called bobbin or spool process. The resulting yarn was then washed, finished, dried without stretch and twisted three turns per inch in the conventional manner.

The properties of the yarn prepared as described above (yarn A) are listed in Table I below, together with those of a yarn (yarn B) spun from the same viscose in the same manner but with a primary bath containing, in addition to 10% sulfuric acid and 0.8% formaldehyde, 26% sodium sulfate, i.e., a regenerating bath.

Table I

Yarn	A	B
Percent Stretch	390	195
T_d	5.9	3.6
T_w	4.0	2.5
T_l	3.0	2.2
E_d	3.0	3.8
E_w	4.0	6.2
E_l	1.0	1.8
G.S	6.1	4.3

It will be seen that, with the use of the dilute, non-regenerating primary bath, it is possible to apply twice the amount of stretch possible with a concentrated, regenerating bath. The resulting yarn has a dry tenacity 2.3 grams/denier higher than that of the control yarn.

EXAMPLE II

A viscose containing 4% cellulose (D.P. 600), 5.5% sodium hydroxide and no coagulation modifier was prepared according to the procedure of Example I, using 50% carbon disulfide and a 3.5 hour xanthation time. This viscose, which contained 31.2% xanthate sulfur, was spun as in Example I into a coagulating bath containing 3.7% sulfuric acid, 10% sodium sulfate and 0.5% formaldehyde at 25° C. Under these conditions, the gel swelling was 5.4. The yarn was stretched 425% in a secondary bath of 2% sulfuric acid and 20% sodium sulfate at 95° C. and given additional stretch to a total of 440% in a tertiary bath of the same composition and temperature. The yarn was treated with a 1% sulfuric acid solution on the final feed wheel to remove excess salt, and wound on a bobbin. The yarn was processed and tested as in Example I, and found to have dry, wet and loop tenacities of 7.5, 5.9, and 3.8 grams/denier, respectively.

EXAMPLE III

Following the general procedure of Example I, two viscoses containing 4% cellulose (D.P. 600) and 5.5% sodium hydroxide were prepared using 50% carbon disulfide. In each case 1% polyethylene glycol having an average molecular weight of 600 was added to the viscose during its preparation. Four different yarns were spun by the procedure of and using the primary bath of Example II, but at different filament deniers (by using spinnerets with different numbers of orifices). The temperature of the primary bath was 25° C.

The yarns were stretched varying amounts in a secondary bath at 95° C. containing 2% sulfuric acid and 20% sodium sulfate and then in a tertiary bath of 1% sulfuric acid at 95° C. The yarns, designated as A, B, C, and D in Table II below, were collected on a bobbin as in Example I except for yarn B which was collected in a relaxed state by allowing it to fall on a tray. All yarns were processed as in Example I.

Table II shows, for each case, the xanthate sulfur content of the viscose, the gel swelling factor of the yarns, the denier per filament and the yarn properties. It will be seen that the dry tenacities were in the extremely high range of 7.2 to 7.7 grams/denier.

Table II

Yarn	A	B	C	D
Percent Xanthate	34.8	32.8	33.5	33.5
Percent Stretch	440	375	405	372
Denier/Filament	.38	.56	.76	1.1
T_d	7.7	7.4	7.5	7.2
T_w	6.0	5.8	5.9	5.7
T_l	3.8	3.9	3.7	2.8
E_d	4.3	5.5	5.5	4.3
E_w	4.8	5.6	5.8	4.3
E_l	1.8	2.5	2.3	1.3
G.S	3.8	3.8	4.4	4.6

EXAMPLE IV

Following the general procedure of Example I, a viscose containing 3% cellulose (D.P. 700 to 800), 5% sodium hydroxide and no coagulation modifier was prepared using 62% carbon disulfide. This viscose, which contained 37.7% xanthate sulfur, was spun as in Example I into a primary bath at 50° C. containing 10% sulfuric acid, no sodium sulfate and 0.8% formaldehyde. The gel yarn was stretched in a secondary bath and then in a tertiary bath, each bath containing 2% sulfuric acid and 20% sodium sulfate and maintained at 95° C. Under these conditions, it was possible to stretch the yarn 382%. When a control yarn was spun from the same viscose under essentially the same conditions, but without formaldehyde in the primary bath, it was only possible to obtain 150% stretch. Table III below shows the properties of these two yarns. It will be seen that, in the presence of formaldehyde, considerably higher dry, wet and loop tenacities were obtained.

Table III

Yarn	Control	Example IV
Percent Stretch	150	382
Denier/Filament	1.1	0.3
T_d	3.8	5.6
T_w	2.1	4.8
T_l	1.5	2.2
E_d	2.8	3.4
E_w	3.1	4.9
E_l	0.3	0.8
G.S	3.4	5.3

EXAMPLE V

A viscose containing 4% cellulose (D.P. 600), 5.5% sodium hydroxide and 1% polyethylene glycol (average molecular weight 1540) was prepared with 44% carbon disulfide. It was spun in the unripened state and at a xanthate sulfur content of 26.7% into a primary bath containing 4% sulfuric acid, 10% sodium sulfate and

0.3% formaldehyde at 25° C. The yarn was stretched as in Example II (two baths) to a total of 315%. The properties of this yarn and those of a control yarn spun from the same viscose under the same conditions but in the absence of fomaldehyde are listed in Table IV.

Table IV

Yarn	Control	Example V
Percent Stretch	98	315
Denier/Filament	0.56	0.56
T_d	4.0	6.6
T_w	2.8	4.5
T_l	2.3	3.2
E_d	4.1	3.7
E_w	4.6	3.7
E_l	1.8	1.5
G.S.	3.9	4.2

EXAMPLE VI

A viscose containing 5% cellulose (D.P. 525) and 6% sodium hydroxide was prepared using 40% carbon disulfide according to the general procedure of Example I. It was spun in an unripened state and at a xanthate sulfur content of 25.5% into a primary bath at 24° C. containing 10% sulfuric acid, no sodium sulfate and 0.8% formaldehyde. The yarn was stretched 430% while it was passed through two regenerating baths at 95° C., each containing 2% sulfuric acid and 20% sodium sulfate. The yarn was processed as in Example I. The properties of this yarn and those of a control yarn spun from the same viscose under the same conditions, but in the absence of formaldehyde are shown in Table V below.

Table V

Yarn	Control	Example VI
Percent Stretch	109	340
Denier/Filament	1.1	1.1
T_d	3.6	6.3
T_w	2.2	3.2
T_l	1.7	2.8
E_d	2.7	4.2
E_w	4.1	3.2
E_l	1.0	1.4
G.S.	3.6	4.4

EXAMPLE VII

A viscose containing 2% of cellulose (D.P. 900 to 1000) and 4% sodium hydroxide was prepared by the general procedure of Example I using 50% carbon disulfide. This viscose having a xanthate sulfur content of 29% was spun into a primary bath at 25° C. containing 4.6% sulfuric acid, 10% sodium sulfate and 0.8% formaldehyde. The coagulated gel yarn was stretched a total of 342% in a regenerating secondary bath at 95° C. containing 2% sulfuric acid and 20% sodium sulfate and in a tertiary bath at 95° C. containing 1% sulfuric acid. The yarn, which had a gel swelling factor of 5.4 and a filament denier of 0.6, was processed as in Example I. It displayed the following tenacities: 7.4 dry, 5.8 wet and 3.9 loop; and the following elongations: 5.0% dry, 5.5% wet and 2.6% loop.

In the process of this invention, a variety of viscoses may be used. They may be prepared from cotton linters or wood pulp or from other cellulose sources or mixtures. The degree of polymerization (D.P.) of the cellulose does not have nearly as great an influence on the level of yarn tenacity as do other variables such as primary bath concentration and composition. However, although the normal cellulose of the industry (D.P. 300 to 400) are suitable, best results (high tenacity combined with good elongation) are obtained with cellulose of D.P. 500 to 1000.

The composition of the viscose may also vary. Cellulose contents from 2% to 8% or more and alkali contents from 4% to 8% or more are satisfactory. Prefered are the dilute viscose solutions, i.e., those containing from 2% to 5% cellulose and from 4% to 6% alkali. In any case, the concentration of the viscose solution must be adjusted in relation to the D.P. of the cellulose to provide a viscose viscosity of 30 to 100 poises.

The alkali cellulose may be completely xanthated in the xanthating churn or xanthated partially in the churn and partially in the mixer. Splitting xanthation so that not over 90% is completed in the churn is described in a copending U.S. patent application, Serial No. 351,592, filed April 28, 1953, now Patent No. 2,801,998, to A. Robertson. In either type of xanthation, conventional or split, it is imperative that the ultimate xanthate sulfur content of the viscose, based on cellulose, be at least 23%, preferably from 25% to 35%. These relatively high xanthate sulfur contents are obtained by using a total of at least 35%, preferably about 40% to about 50% carbon disulfide (based on cellulose).

The viscose, after being filtered and deaerated, is preferably spun in an unripened condition, i.e., at a salt index exceeding 7 and usually much higher. It is one of the advantages of this invention that unripened viscose solutions can be used, thereby saving ripening time and equipment. However, viscose prepared with large amounts of carbon disulfide, e.g., 55% to 65%, are advantageously slightly ripened to bring the xanthate sulfur content within the optimum range.

As illustrated in the examples, coagulation modifiers which are effective in baths free of heavy metal salts such as zinc salts can be added to the viscose. These modifiers include the previously described ethers and polyethylene oxides. The ethers include such compounds as phenoxyethanol, ethoxyethanol, methoxyethoxyethanol, butoxyethoxyethanol, phenoxyethoxyethanol, ethoxyethoxyethoxyethanol, butoxyethoxyethoxyethanol, phenoxyethoxyethoxyethanol, butoxyethoxyethoxyethoxyethanol, phenoxyethoxyethoxyethoxyethanol, 1-ethenyloxy-2-methoxyethylene, ethylene glycol diethyl ether, triethylene glycol diethyl ether, tetramethylene glycol diethyl ether, triethylene glycol dimethyl ether, diethylene glycol diethyl ether, etc. The polyethylene oxides are those of the formula $RO(CH_2CH_2O)_nH$, where n is at least equal to 4, i.e., polymers which have a molecular weight of at least about 200, and which in addition have the necessary solubility in viscose. Those polyethylene oxides having molecular weights between about 300 and about 2000 are preferred. It should be understood that it is possible, and sometimes desirable, to use mixtures of two or more of the above-described coagulation modifiers. In any case, the total concentration in the viscose should be between about 0.5% and 2%. Optimum results are obtained with concentrations between 0.75% and 1.5%. The use of these specific coagulation modifiers leads to yarns having somewhat increased tenacities and elongations as compared with yarns prepared in the absence of modifiers.

The viscose spinning solution is then extruded into the primary bath. The viscose may be at the normal ambient temperature, 18° C. to 25° C., or it may be heated to 40° C. to 50° C. or higher prior to spinning. The primary bath is desirably at a temperature not exceeding 50° C. The preferred primary bath temperature is 25–50° C., and the normal ambient temperature, e.g., 18–25° C., can be used. The primary bath is an aqueous acidic coagulating bath, having generally a pH between 1 and 2. It is non-regenerating because of the presence of formaldehyde. It is believed that formaldehyde stabilizes the xanthate groups by forming cellulose hydroxymethyl xanthate. This compound is relatively stable even at low pH, but its formation in substantial amounts requires rapid penetration of the gel filament by the formaldehyde. It is believed that rapid penetration is made possible by maintaining the total electrolyte (sulfuric acid and sodium sulfate, particularly the latter) concentration in the primary bath at a sufficiently low level. In affirming this theory, I have found that the sum of the concentrations

(based on the weight of the primary bath) of sulfuric acid and sodium sulfate should be in the range of 8% to 16%. Of these two ingredients, sulfuric acid should always be present in amounts between about 2% and about 11%. With less than this amount, the primary bath does not have a sufficiently rapid coagulating action. With more than this amount the regenerating effect (decomposition of the xanthate groups) becomes too great to permit the desired high stretching in a subsequent step. As shown in the examples, I have also found that it is permissible to dispense with sodium sulfate altogether. Furthermore, I believe that salts of heavy metals, i.e., of metals of specific gravity above 4 such as zinc sulfate, iron sulfate or chromium sulfate, retard the penetration of formaldehyde. Therefore, the presence of these salts should be avoided. By adhering to the above limitations on the primary bath above 70%, and generally nearly 100% of the xanthate groups originally present in the viscose remain undecomposed at the time the gel filament enters the secondary (regenerating) bath. This compares to the primary baths of the prior art wherein, not more than 20% to 35% of the original xanthate groups are still intact when the filament enters a secondary bath.

The best results are obtained where the primary bath contains both sulfuric acid and sodium sulfate, the first one in the range of 3 to 6% and the second one in the range of 8 to 12%, provided always the sum of these concentrations is in the range of 8 to 16%.

Another effect of the low total acid-salt concentration and the absence of heavy metal salts in the primary bath is to form coagulated filaments having relatively high gel-swelling factors. This permits the use of a larger number of spinneret holes to produce finer filaments than can be produced with conventional, more concentrated spinning baths. In general, the gel-swelling factor of the yarns obtainable by this process lies between 3.5 and 6.2, high enough to permit spinning of fine denier filaments and still low enough to provide optimum yarn properties. This is contrary to the teachings of recent art on high tenacity yarn manufacture (see U.S. Patent 2,535,044) where very low gel-swelling factors (within the range of 2.5 to 3) were preferred.

The relatively highly swollen state of the filaments of this invention also seems to permit rapid penetration of formaldehyde to effect stabilization of the xanthate groups. Therefore, small amounts of formaldehyde (0.2% to 1.0% and preferably between 0.3% to 0.8%) can be used successfully. In fact, the use of more than about 1% of formaldehyde in the coagulating bath is undesirable since the yarn then becomes too highly plasticized and less tension can be applied to it. The optimum amount of formaldehyde varies with the spinning speed, more being desirable at the higher speeds. The formaldehyde should contact the yarn before any appreciable stretch is applied to the yarn. However, the formaldehyde should not be applied to the yarn before coagulation has begun. Thus, if the formaldehyde is mixed with the viscose prior to extrusion, it has been found that the stretchability of the yarn is not increased and the desired results are not achieved.

After leaving the primary bath, the filaments are passed through at least one secondary bath ("hot dip" bath or stretching bath) which has a regenerating action on the cellulose xanthate, i.e., decomposes the xanthate groups. The secondary bath may consist simply of aqueous sulfuric acid in concentrations of about 1% to 4%, or it may also contain a dehydrating salt, preferably sodium sulfate, in concentrations of 2% to 25%. The presence of salt in the secondary bath tends to prevent over-plasticization and sticking of filaments. The secondary bath should be free from formaldehyde except for the very small amounts which may be carried from the primary bath. It should also be free of added heavy metal salts. If desired, a second regenerating bath or tertiary bath may be used. This bath is also an aqueous sulfuric acid bath which may or may not have the same composition as the secondary bath. For best results, the secondary bath or baths should be at a temperature above 80° C., preferably between 90° C. and the boiling point of the aqueous solution used.

The normal spinning procedure is to draw off the freshly coagulated gel yarn in the primary bath with a feed wheel speed equal to or less than the jet velocity, so that no stretch is applied in the primary bath. All the stretch should be applied in the secondary bath or baths between positively driven rollers traveling at different speeds. Normally, the yarn travels about 5 to 30 inches in the primary bath and about 10 to 30 inches in the secondary bath system. Stretch is applied in the secondary bath or baths to the extent of at least 300% and up to 450% or more, of the unstretched length of the yarn. Such extraordinarily high stretches are possible because they are applied to the coagulated, but substantially non-regenerated yarn as described. The desirable operating tension on the yarn is between 60% and 90% of the breaking tension.

The bobbin process has been used in most of the examples but it is immaterial whether spinning is done by the bobbin, bucket or continuous processes. It is possible to realize some increase in elongation without undesirable sacrifice of tenacity by collecting the yarn in the relaxed state on a tray or platform.

Following spinning, the yarn is washed free of acid and salt and then dried under tension, according to conventional procedures. If preferred, the yarn may be twister- or slasher-dried to enable the dry elongation of the finished product to be controlled.

Spinning may also be carried out with the aid of spinning tubes such as described in Millhiser U.S. Patent 2,440,057 or in Drisch et al. U.S. Patent 2,511,699. These tubes of relatively small diameter and of substantial length confine the filaments in their critical stage of formation. By maintaining the speed of the cocurrent bath-flow through the tube only slightly below the speed of the filament bundle passing through the tube, no substantial tension is imposed on the filaments. It is thus possible to increase materially the rate of spinning without substantial sacrifice in yarn properties. Spinning speeds can vary from the 25 to 30 yards per minute used in small scale, experimental equipment to 100 yards per minute or more used in industrial processes.

This invention makes it possible to prepare low filament denier yarns with strengths considerably higher than considered possible heretofore. The yarns are produced using less chemicals in the bath than previously used and at practical spinning speeds.

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. The yarns are particularly desirable for use in sheer wearing apparel where superior strength is desired; in industrial applications such as filter cloths, strainers, etc.; in the preparation of non-woven fabrics by forming mats imbedded in thermo-setting resins; in laminates having layers of fabric between layers of plastics; and in the bulk polymerization of vinyl monomers to produce fiber-reinforced moldings.

As many widely different embodiments may be made without departing from the spirit and scope of the invention, it is understood that the invention is not limited except as defined in the appended claims.

The invention claimed is:

1. A process for the production of high tenacity regenerated cellulose filaments which comprises extruding a xanthated viscose spinning solution, the xanthated viscose containing at least 23% xanthate sulfur based on the cellulose content, through a plurality of orifices into an aqueous coagulating bath free of heavy metal salts and containing by weight about 0.2% to 1.0% formaldehyde, from 2% to 11% sulfuric acid and up to 12%

sodium sulfate, the sum of sulfuric acid and sodium sulfate concentrations being from 8% to 16%, to form filaments containing at least 70% of the xanthate groups originally present in the viscose, and stretching the coagulated filaments at least 300% while passing them through at least one aqueous regenerating bath containing a major percentage of water and a minor percentage of sulfuric acid.

2. A process as in claim 1 wherein the coagulated filaments are stretched 300% to 450% while passing through at least one aqueous regenerating bath containing 1% to 4% sulfuric acid to form filaments of up to 1.5 denier/filament.

3. A process as in claim 1 wherein the viscose spinning solution contains from 2% to 8% cellulose, from 4% to 8% alkali and has a xanthate sulfur content of at least 23% based on the weight of cellulose in the viscose solution.

4. A process as in claim 1 wherein the viscose solution contains 0.5% to 2% of an alkali-soluble coagulation modifier selected from the group consisting of (A) ethers of the formula $RO—(CH_2CH_2O)_n—R'$, where R is selected from the group consisting of alkyl and aryl, n is an integer from 1 to 4 and R' is selected from the group consisting of hydrogen, alkyl and aryl and (B) polyethylene oxides of molecular weight between 200 and 2000.

5. A process is in claim 1 wherein the viscose solution contains 0.75% to 1.5% of an alkali-soluble coagulation modifier selected from the group consisting of (A) ethers of the formula $RO—(CH_2CH_2O)_n—R'$, where R is selected from the group consisting of alkyl and aryl, n is an integer from 1 to 4 and R' is selected from the group consisting of hydrogen, alkyl and aryl and (B) polyethylene oxides of molecular weight between 200 and 2000.

6. A process for the production of high tenacity regenerated cellulose filaments which comprises extruding a xanthated viscose spinning solution, the xanthated viscose containing at least 23% xanthate sulfur based on the cellulose content, through a plurality of orifices into an aqueous coagulating bath free of heavy metal salts and containing by weight about 0.3% to 0.8% formaldehyde, from 3% to 6% sulfuric acid and 8% to 12% sodium sulfate, the sum of sulfuric acid and sodium sulfate concentrations being from 8% to 16%, to form filaments containing at least 70% of the xanthate groups originally present in the viscose, and stretching the coagulated filaments at least 300% while passing them through at least one aqueous regenerating bath containing a major percentage of water and a minor percentage of sulfuric acid.

7. A process as in claim 6 wherein the coagulated filaments are stretched 300% to 450% while passing through at least one aqueous regenerating bath containing 1% to 4% sulfuric acid to form filaments of up to 1.5 denier/filament.

8. A process as in claim 6 wherein the viscose spinning solution contains from 2% to 8% cellulose, from 4% to 8% alkali and has a xanthate sulfuric content of at least 23% based on the weight of cellulose in the viscose solution.

9. A process as in claim 6 wherein the viscose solution contains 0.5% to 2% of an alkali-soluble coagulation modifier selected from the group consisting of (A) ethers of the formula $RO—(CH_2CH_2O)_n—R'$, where R is selected from the group consisting of alkyl and aryl, n is an integer from 1 to 4 and R' is selected from the group consisting of hydrogen, alkyl and aryl and (B) polyethylene oxides of molecular weight between 200 and 2000.

10. A process as in claim 6 wherein the viscose solution contains 0.75% to 1.5% of an alkali-soluble coagulation modifier selected from the group consisting of (A) ethers of the formula $RO—(CH_2CH_2O)_n—R'$, where R is selected from the group consisting of alkyl and aryl, n is an integer from 1 to 4 and R' is selected from the group consisting of hydrogen, alkyl and aryl and (B) polyethylene oxides of molecular weight between 200 and 2000.

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