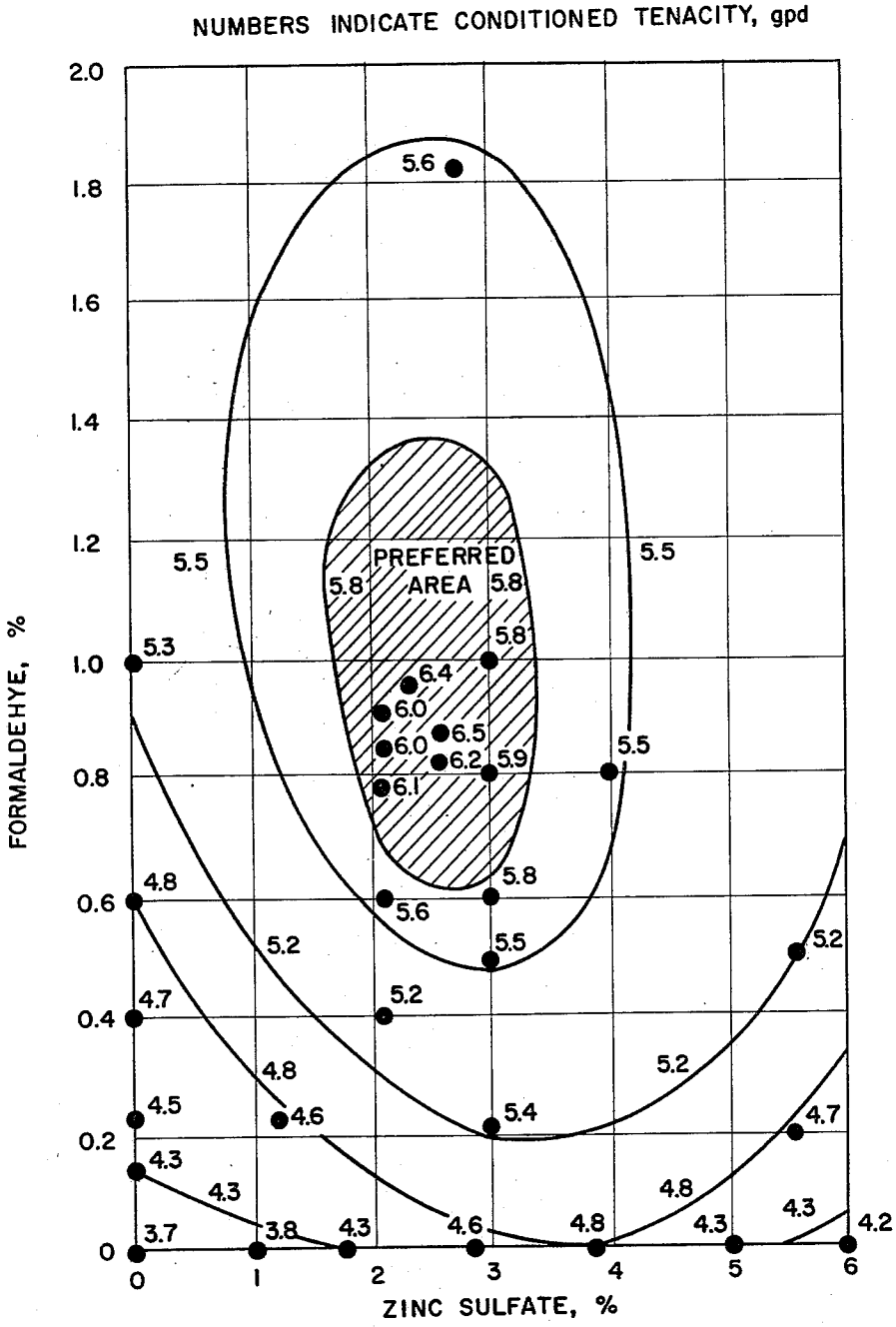
METHOD FOR PRODUCING HIGH TENACITY RAYON

Original Filed July 20, 1965 3 Sheets-Sheet 1

FIG. 1

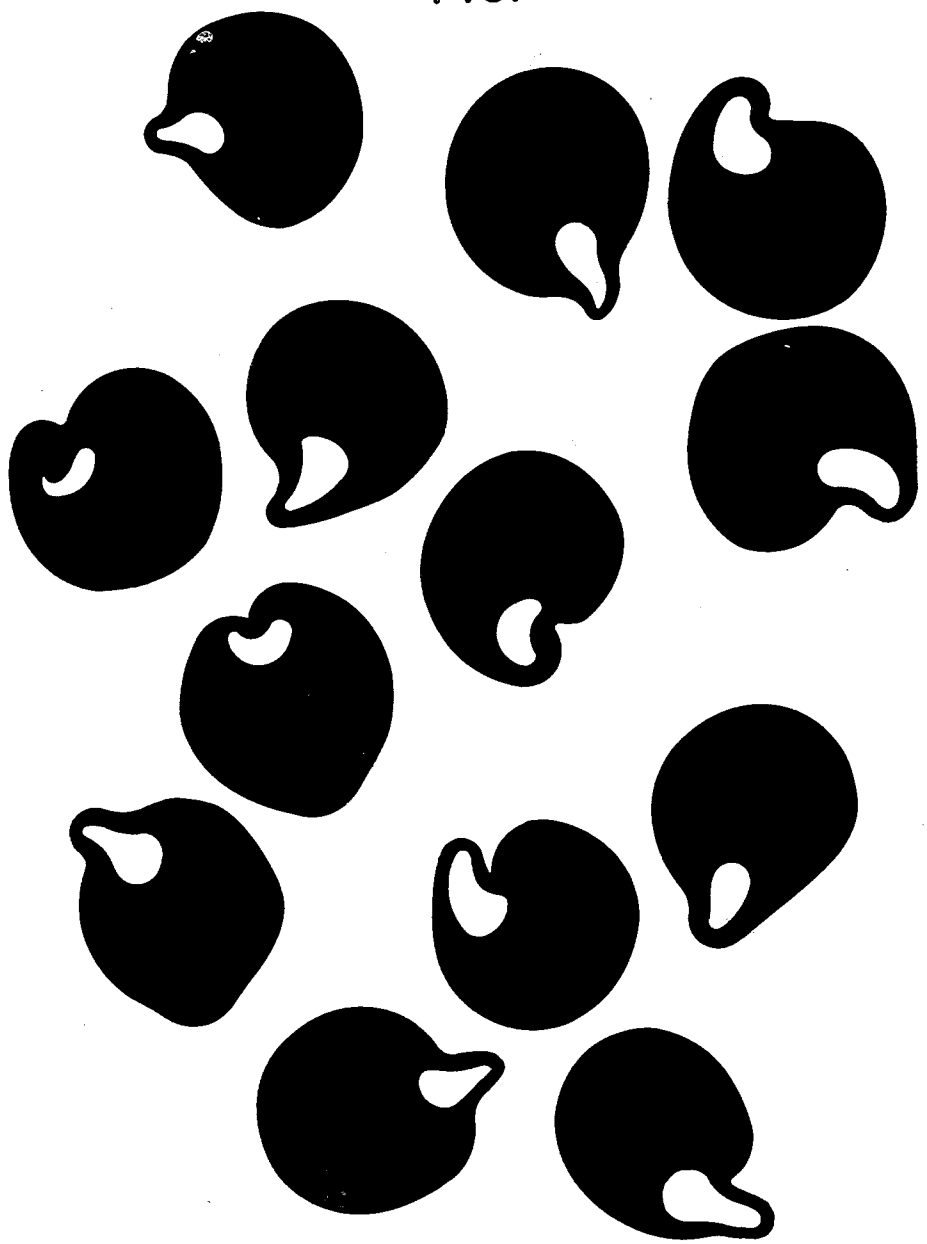


INVENTORS
HUGH D. STEVENS
ROBERT B. KENNEDY
GEORGE C. DAUL
BY Pennie, Edmonds, Morton, Taylor and Adams
ATTORNEYS

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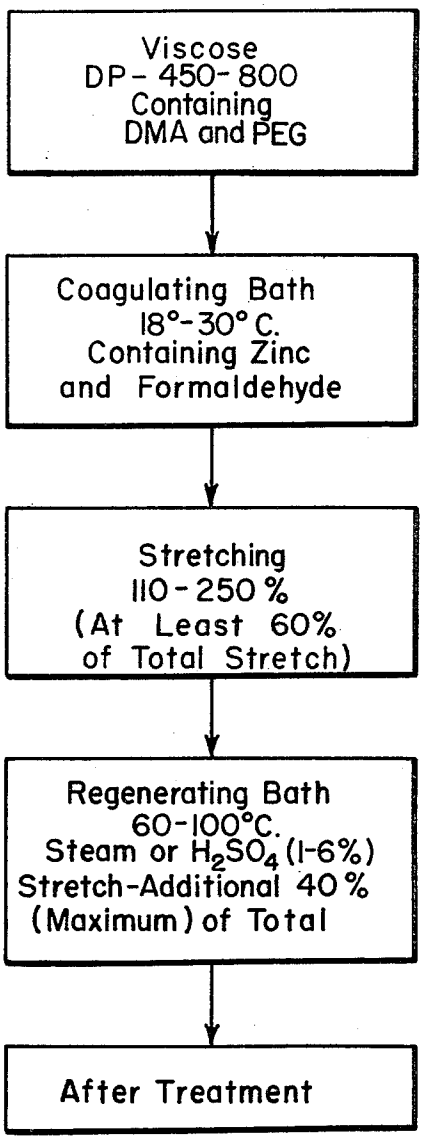
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FIG. 2



INVENTORS
HUGH D. STEVENS
ROBERT B. KENNEDY
GEORGE C. DAUL
BY Pennie, Edmonds, Morton
Taylor and Adams
ATTORNEYS

FIG. 3



INVENTORS
HUGH D. STEVENS
ROBERT B. KENNEDY
BY GEORGE C. DAUL
Pennie, Edmonds Morton, Taylor and Adams
ATTORNEYS

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METHOD FOR PRODUCING HIGH TENACITY RAYON

Hugh D. Stevens, Flanders, Robert B. Kennedy, Rockaway, and George C. Daul, Morristown, N.J., assignors to ITT Rayonier Incorporated, a corporation of Delaware

Continuation of application Ser. No. 473,321, July 20, 1965. This application Feb. 24, 1969, Ser. No. 805,969
Int. Cl. D01f 3/28, 3/12; D01d 5/12
U.S. Cl. 264—197 3 Claims

ABSTRACT OF THE DISCLOSURE

Rayon filaments having a conditioned tenacity of about 6 g.p.d., a wet modulus of 1 to 2 g.p.d., a wet tenacity of 3 to 5 g.p.d. and an elongation of from 8 to 12% are prepared by (a) extruding a viscose solution having a gamma number of 40 to 90, a salt index of 7.5 to 12 and containing a mixed modifier, which substantially retards regeneration (b) into an acidic coagulating bath at a temperature of from 18 to 30° C., the bath containing from about 0.2 to 2% by weight formaldehyde and from about 1 to 6% by weight zinc sulfate. The resulting coagulated filaments are stretched from about 110 to 250% in length prior to substantial regeneration, and are stretched at least an additional 30% in length during regeneration in one or more hot regeneration baths at a temperature of about 60° C. to 100° C.

This application is a continuation of application Ser. No. 473,321, filed July 20, 1965.

In recent years several methods for increasing the tenacity and improving the other properties of viscose rayon filaments have been developed until now conditioned (dry) tenacities as high as 3 to 6 grams per denier (g.p.d.) are fairly common. This relatively high conditioned tenacity range has been attained by using cellulose material having a relatively high degree of polymerization (D.P.), decreasing and even eliminating aging and ripening steps when preparing alkali cellulose and viscose, adding modifiers such as surfactants and retardants to the viscose solution and/or the spin-bath and stretch-spinning retarded viscose solutions at relatively slow speeds and high gamma numbers into multiple spinbaths. While such variations in materials and processing conditions have yielded substantial improvement in conditioned tenacities it has always been at the expense of other desirable properties of the filament such as its elongation, flexibility and toughness. The problem has been to obtain a filament having a high conditioned tenacity that also has a high wet modulus, good elongation, high wet tenacity and above all is still flexible and not brittle. None of the presently known processes provide such a combination.

After an intensive investigation we have discovered a critical combination of processing variables that provides filaments having exceptionally high conditioned tenacity, high wet modulus, high wet tenacity, good elongation and that are still flexible and non-brittle. The filaments of the invention have an average conditioned tenacity of about 6 g.p.d., a wet modulus of 1 to 2 g.p.d., a wet tenacity of 3 to 5 g.p.d., an elongation of from about 8 to 12 percent and high flexibility. In addition the filaments have a solubility in 6.5 percent sodium hydroxide solution of

less than 4.5 percent by weight. They also have a unique cross-sectional shape that is evident when viewed under high magnification (see FIGURE 2). Substantially, all the individual filaments as spun are round and smoothly curved except for a pointed protuberance on one side. This shape is advantageous in that the protuberances effect a sharp reduction in slippage of individual fibers when the same are combined to form threads, cords and staple yarns.

The process of the invention comprises preparing a viscose solution from cellulose xanthate having a relatively high degree of polymerization, containing a mixture of modifiers and having a high gamma number, spinning the viscose in a cold acid spin bath containing both formaldehyde and a zinc salt to effect coagulation, while the filaments are in a state of coagulation and up to regeneration subjecting the filaments to the major part of the total stretching, regenerating the filaments, and after regeneration stretching the filaments an additional but minor part of the total stretch.

The formation of a suitable high D.P. modified viscose spinning solution suitable for use in the process of the invention has been described in U.S. Patent No. 2,942,931 that issued June 28, 1960. Such spinning solutions are formed from cellulose xanthate having a relatively uniform chain length with a D.P. of from about 450 to 800, a suitable balanced ratio of cellulose and sodium hydroxide within the range of about 4 to 9 percent in the viscose and from about 32 to 44 percent carbon bisulfide based on cellulose in alkali cellulose. In the process purified chemical cellulose such as bleached sulfite and prehydrolyzed kraft wood pulps as well as cotton linters having relatively high uniform D.P. are converted into alkali cellulose and xanthated with 32 to 44 percent carbon bisulfide at ambient temperatures in the usual manner.

The viscose is modified with a mixed modifier comprising from 1.0 to 3.0 percent dimethyl amine (DMA) and from 0.5 to 2.5 percent polyethylene glycol (PEG) on the weight of the cellulose which may be added at any stage prior to spinning but preferably during either mixing or deareation. The salt (NaCl) index of the spinning solution should be between about 7 and 12 (preferably between 9 and 11) and the gamma number between about 40 and 90 (preferably between 50 and 80) when spun with ripening selected to attain this level. The salt index and gamma number, of course, depend upon the amount of carbon bisulfide used in xanthation, the temperature of the reaction and the amount of ripening used.

The viscosity of the spinning solution is not particularly critical and can range between about 20 to 150 ball fall seconds (b.f.s.). This is an advantageous viscosity level since most processes for spinning high tenacity filaments require high viscosities (up to about 400 b.f.s.) to produce satisfactory high tenacity fiber. High viscosity makes accurate denier control difficult and interferes with deaeration, pumping and spinning processes.

In the process of the invention the modified spinning solution is spun at 18 to 30° C. (preferably 20 to 25° C.) and a take-up speed of 20 to 60 meters per minute into a coagulating-type spinbath containing 0.2 to 2.0 percent formaldehyde, 1 to 6 percent zinc sulfate, 3 to 9 percent sulfuric acid and from 7 to 18 percent sodium sulfate. The spinbath may also contain from 0.01 to 0.1 percent of a surface active agent or lubricant such as lauryl pyridinium chloride (LPC) and the like. Travel of the filament through this bath should be limited to that required to

develop sufficient strength for stretching in order to avoid any unnecessary regeneration. While the distance from spinerette to emergence from the bath can vary from about 4 to 48 inches or more, depending upon spinning speed, composition of the viscose, etc., less than 25 inches will usually be sufficient. We have found, for example, that 12 to 15 inches immersion is optimum for spinning speeds of 25 to 30 meters per minute at wind-up.

Almost immediately after leaving the coagulating bath the filaments as a group or tow (still completely soluble in dilute alkali) are stretched from about 110 to 250 percent or an amount equivalent to not less than about 60% of the total stretch they are to receive. To effect this stretch the tow is drawn from the bath at the desired disance, passed around a driven godet and then several times around two or more godets driven at a sufficiently greater speed to provide the desired continuous stretching. As indicated above, in the process of the invention the filament will receive from about 180 to 300 percent total stretch of which about 110 to 250 percent or not less than about 60 percent takes place before any substantial regeneration of said filament.

Since filaments made by the procedures described above are rubbery and relatively strong immediately upon extrusion into the coagulation bath, it is important to stretch as quickly and as much as possible prior to regeneration in order to obtain the desired high wet modulus. The strongest filaments with the highest wet modulus are produced when the stretching takes place within one or two seconds after the onset of coagulation. For example, when only two stretch rolls are used, most of the stretching occurs on or as the tow leaves the first roll. The stretching is then completed as the tow of filaments passes through the air in contact with adhering spinbath on its way to and through the regeneration bath or baths.

To regenerate the coagulated filament tow it is conducted through one or more hot regeneration baths which may be either hot dilute acid or steam. While steam baths can be used we prefer dilute acid baths for our purpose at 60 to 100° C. (preferably about 80° C.) containing from about 0.5 to 5.0 percent sulfuric acid (preferably about 3.0 percent) and a stabilized modicum of the salts carried over from the preceding coagulation bath. During regeneration the filament receives the balanec of the total stretch amounting to not more than about 40 percent of the total amount of stretch to the filaments. The combination of PEG–DMA mixed modifier in the viscose and zinc and formaldehyde in the coagulating bath using the indicated spinning conditions affords sufficiently rapid coagulation of the filament prior to regeneration to permit the indicated high stretch and relatively high spinning speeds that are higher than are normal in the production of high wet modulus fibers. We have found that take-up speed up to 50 to 60 meters per minute are entirely feasible using the process of the present invention without any substantial loss of desirable filament properties.

After regeneration the filaments are desulfurized and processed as continuous filament rayon or alternatively cut into staple fiber and processed by procedures common to the art as desired. Relaxing of the filament after regeneration is also generally beneficial. This can be accomplished as a separate step or advantageously in conjunction with desulfuring and since the regenerated fiber of tne invention is relatively insoluble in caustic a warm 1 percent aqueous solution of sodium hydroxide can be used to assist in said relaxing.

The following examples illustrate the invention in more detail.

EXAMPLE I

A modified viscose spinning solution of the invention was prepared as follows: a high quality, bleached, southern pine prehydrolyzed kraft wood pulp was steeped in concentrated cold caustic solution, pressed and shredded in the usual manner to provide a high DP, uniform alkali cellulose containing 35 percent cellulose and 15 percent sodium hydroxide. The alkali cellulose was then xanthated with 38 percent carbon bisulfide on the cellulose for 100 minutes at 29° C. and converted into a viscose solution containing 4.8 percent cellulose and 5.8 percent sodium hydroxide. 2.4 percent DMA and 1.7 percent PEG on the cellulose were added and the modified viscose mixed for 2 hours at 10° C. until the desired salt index and gamma number for spinning were obtained. Tows composed of filaments having an average denier of 1.5 were then obtained by spinning the foregoing solution through a spinnerette having 1100 holes each of 0.002 inch diameter under the following conditions:

SAMPLE A

A sample of the viscose spinning solution having a salt index of 10 and a gamma number of 56, obtained by ripening said viscose for 16 hours at 10° C. was warmed to 21° C. and spun into a coagulation spinbath containing 7 percent sulfuric acid, 18 percent sodium sulfate, 3 percent zinc sulfate, 0.8 percent formaldehyde, 75 p.p.m. LPC and 0.25 percent DMA. The tow was removed from the bath after 12 inches immersion, wrapped three times around a godet to prevent slippage and then around a second godet driven at sufficient speed to provide 225 percent stretch. It was then passed through a regeneration spinbath at 80–100° C. containing about 3 percent sulfuric acid and small amounts of sodium sulfate and formaldehyde carried over from the coagulation bath and stretched an additional 45 percent (20 percent of the total), desulfurized, washed, cut, finished and dried in the usual manner. The result was a typical high wet modulus fiber of the present invention whose properties are listed under A in Table 1 below.

CONTROL SAMPLE B

A second sample of the spinning solution used in Sample A was spun in exactly the same manner at the same salt index and through the same equipment into a 21° C. coagulation bath having the following composition: 6.5 percent sulfuric acid, 10 percent sodium sulfate, no zinc sulfate, 1.0 percent formaldehyde, 75 p.p.m. LPC and 0.25 percent DMA. The resultant filament was then coagulated, regenerated and finished in exactly the same manner as Sample A. The properties of the same are listed under B in Table 1 below.

CONTROL SAMPLE C

A third portion of the same viscose solution used in Samples 1 and 2 was spun into the following coagulating bath under the indicated conditions:

The temperature of the coagulation bath was increased to 30° C., and its composition was 7 percent sulfuric acid, 3.5 percent zinc sulfate, no formaldehyde, 10 percent sodium sulfate, 75 p.p.m. LPC and 0.5 percent DMA. The regeneration bath was exactly the same as before but the immersion length in the coagulation bath was increased to 15 inches while the take-up speed remained at 25 meters per minute. The maximum total stretch possible was only 150 percent. The properties of the resultant fiber are listed under C in Table 1 below.

CONTROL SAMPLE D

A fourth portion of the viscose solution used in the preceding samples was ripened to a salt index of 8.0 and gamma number 40 and then spun into fiber as before under the following conditions:

The temperature of the coagulation bath was increased to 60° C. and its composition changed to 7 percent sulfuric acid, 18 percent sodium sulfate, 6.0 percent zinc sulfate, no formaldehyde, 75 p.p.m. LPC and 0.5 percent DMA. Bath travel was increased to 40 inches while the speed was maintained at 25 meters per minute but the maximum total stretch possible was only 100 percent. The regeneration and other treatments were the same as

in the preceding samples. The properties of the resultant fiber are listed under D in FIGURE 1, below.

SAMPLE E

Sample A was duplicated in every detail except that the bath travel was increased to 20 inches and the take-up speed to 40 meters per minute.

The properties of the resultant fiber are listed under E in Table I, below.

TABLE I

Property	Sample A	B	C	D	E
Cond. tenacity, g.p.d.	6.5	4.8	4.6	4.8	6.0
Cond. elongation, percent	10.2	6.5	12.3	22.5	9.5
Wet tenacity, g.p.d.	4.8	3.2	3.2	3.4	4.6
Wet elongation, percent	10.8	6.5	17.1	28.0	10.4
Wet modulus (at 5% extension), g.p.d.	1.5	2.2	0.65	0.17	1.6
Water retention, percent	66	62	70	76	66
Solubility in 6.5% NaOH at 20° C.	4.5	8.0	16.0	36.0	4.4

To be especially noted in the results of Table I are the superior physical properties in the two Samples A and E made by the conditions of this process compared with those of the control Samples B, C, and D.

While the wet modulus of Sample B (made without zinc sulfate in the coagulation bath) is high, the low elongation or extensibility of the fiber indicates brittleness and is too low to give good processability in textile processing.

Sample C (made without formaldehyde) has a mediocre wet modulus and much higher NaOH solubility, while Sample D (made with ripened viscose with relatively low salt index and gamma number) has a low modulus and high NaOH solubility. Both of these fibers would be subject to damage under alkaline textile processing conditions such as in alkaline scouring or in mercerization. All three control fibers have much lower conditioned and wet tenacities than the fibers of this invention.

EXAMPLE II

A high quality, high D.P. pulp with uniform chain length was used to prepare alkali cellulose containing 35% cellulose and 15% NaOH. The alkali cellulose was xanthated with 38% CS_2 (on cellulose) for 100 minutes at 28–30° C.

A viscose was prepared from this xanthate to have a composition of 5.5 cellulose, 6.0 NaOH to which was added 2.4% dimethylamine and 1.7% Carbowax 1540 on the weight of cellulose. It was mixed for 2 hours at 10° C., filtered, deaerated and maintained at 10° C. (to retard ripening) for 16 hours. It had a salt index of 11 and viscosity of 42 b.f.s.

The viscose was spun at 21° C. through a spinnerette with 3000 holes of .0030" diameter into a spin bath containing 6.25% H_2SO_4, 10% Na_2SO_4, 0.85% HCHO, 2.2% $ZnSO_4$, 75 p.p.m. LPC, 0.25% DMA, and maintained at a temperature of 20–22° C.

The filament tow was removed from the bath 20" from the spinnerette, wrapped three times around the first godet (to prevent slippage), then over a second godet driven at a faster rate than the first godet, stretched 218% between the first and second godets, thence passed through a regenerating bath containing about 3.5% H_2SO_4 and equilibrium amounts of Na_2SO_4 and HCHO carried over from the primary bath and maintained at 85–97° C. The tow was stretched about 175% during coagulation and about 43% during regeneration.

A 2.5 denier fiber was produced with tenacity of 6.0 g.p.d. conditioned, 4.5 g.p.d. wet, wet modulus of 1.8 g.p.d at 5% elongation and solubility in 65% NaOH at 20° C of 3.5%. The D.P. was 650.

EXAMPLE III

A viscose prepared as in Example II was spun through a spinnerete with 1100 holes of 0.0025" in diameter into a bath of the same composition as that used in Example II.

The coagulating bath temperature was varied from 15° C. to 50° C. while regeneration bath conditions were maintained constant.

From the following table it may readily be seen that best fiber properties were obtained between 20° and 25° C. and they correlate with stretchability of the coagulated yarn. As bath temperature was increased above 30° C., total stretch decreased and fiber properties including conditioned and wet tenacity and wet modulus deteriorated progressively.

Bath Temp.	Total stretch, Percent	Conditioned tenacity, g.p.d.	Wet tenacity, g.p.d.	Wet modulus, g.p.d.
15°	(Would not spin)			
17°	(Spun poorly, irregularly)			
18°	180	5.0	4.0	1.8
20°	210	6.5	4.8	2.0
22°	225	6.8	5.2	2.2
25°	210	6.2	4.5	1.8
30°	190	5.7	4.0	1.5
40°	162	5.0	3.7	0.8
50°	150	4.5	3.4	0.5

EXAMPLE IV

A viscose was prepared as in Example I, pumped through a spinnerette of 1100 holes each of 0.0002" diameter into a bath containing 6.25% H_2SO_4, 9.5% Na_2SO_4, 2.5% $ZnSO_4$, 0.9% HCHO, 75 p.p.m. LPC, 0.25% DMA at a temperature of 21° C.

The filament tow was removed from the bath 12" from the spinnerette, wrapped on the first godet (to prevent slippage), then over a second godet traveling at a faster rate than the first godet, stretched between the first and second godets 220% and passed through a regenerating bath as in Example I.

The finished fiber had average tenacity of 6.5 g.p.d. conditioned, 5.2 g.p.d. wet, wet modulus of 2.5 and high knot and loop strength. Some individual filaments had tenacities as high as 8 g.p.d.

EXAMPLE V

The conditions of Example IV were used except that hot water (90° C.) was applied to the tow at the first godet to start regenerating of the cellulose, where only coagulation takes place on the process of this invention, a sample was collected, then the hot water was applied further along the tow in 6" progressive steps up to the regeneration bath. Samples representative of each condition were collected and tested.

In contrast to the excellent fiber properties obtained in Example IV, when the hot water was applied on the No. 1 godet (nearest the point of emergence of the tow from the coagulating bath), allowable stretch was reduced to 165% resulting in a loss in fiber tenacity of about 2 g.p.d. A wet modulus of less than 1 g.p.d. was obtained. As the hot water was moved farther away from the first godet and closer to the final stretch roll, physical properties improved accordingly, with fully acceptable properties of about 6 g.p.d. reached only after the point at which the tow had been stretched 180%, that is 80% of the maximum attainable (220%) under these conditions.

This example proves that cellulose regeneration should not be initiated to any significant amount, if at all, prior to stretching of the tow an amount of at least 60% of the total allowable to obtain the superior fibers of this invention.

EXAMPLE VI

A viscose was made as in Example I except that 34% CS_2 was used. The NaCl index at spin was 8.0 and

viscosity, 35 ball fall seconds. It was spun under the same conditions used in Example IV except that maximum allowable stretch was 190%.

The finished fiber had average tenacities of 5.6 g.p.d. conditioned, 4.2 g.p.d. wet and 1.4 g.p.d. wet modulus at 5% elongation.

EXAMPLE VII

A high quality, high D.P. pulp with uniform chain length was used to prepare alkali cellulose containing 35% cellulose and 15% NaOH and aged to a D.P. of about 650. It was xanthated with 37% CS_2 (based on cellulose) for 100 minutes at 29–30° C.

Viscose was prepared from this xanthate to have a composition of 5.5% cellulose, 6.0% NaOH to which was added 2.4% dimethylamine and 1.7% polyethylene glycol, M.W. 1500 (on the weight of cellulose). It was mixed for 2 hours at 10° C., filtered, deaerated and divided into 2 portions.

(A) One part was passed through a coil to equilibrate to about 22° C. and spun immediately into a coagulating bath containing 6.4% H_2SO_4, 9.8% Na_2SO_4, 2.3% $ZnSO_4$, 0.9% HCHO, 75 p.p.m. lauryl pyridinium chloride, 0.25% dimethylamine and maintained at a temperature of 26° C.

The tow, spun at 25 m./m. was removed from the coagulating bath 15 inches from the spinnerette, wrapped three times on the first godet and then around a second godet driven at greater speed (to stretch the two 220%) and passed through a regenerating bath containing about 3% H_2SO_4 and carry-over amounts of salts and formaldehyde, and maintained at 80–100° C. Approximately 70% of the total amount of stretch took place prior to regeneration.

The usual cutting, desulfurizing, washing, finishing and drying procedures were performed. Physical properties of the fibers obtained are showing under "A" below.

(B) The second portion of viscose described above was held at 10° C. overnight (16 hours), equilibrated to spinning temperature and then spun under the same conditions described above. Stretch applied to the tow was 213%.

Results:

	A	B
Viscose:		
NaCl index	11.4	11.2
Ball fall viscosity (secs.)	42	38
Xanthate sulfur, percent	1.23	1.06
Fiber properties, denier	1.4	1.4
Conditioned:		
Tenacity, g.p.d	7.0	6.8
Elongation, percent	9.5	9.3
Wet:		
Tenacity, g.p.d	5.0	5.0
Elongation, percent	11.3	11.1
Modulus at 5% extension g.p.d	1.7	1.7

These results show that the viscose containing amine and PEG modifiers is quite stable under the conditions used and may be spun after minimum "ripening" or after extended "ripening" at low temperature. Excellent fiber physical properties were obtained in both cases.

EXAMPLE VIII

A viscose was prepared using conditions identical to those of Example VII except that no dimethylamine or polyethylene glycol (modifiers) were added. It was divided into two parts, A and B, and spun as in the foregoing example.

The tow produced from the unripened viscose (A) could be stretched only 170% and the viscose (B) ripened overnight produced a tow which could be stretched only 150%.

Results:

	A	B
Viscose:		
NaCl index	11.6	11.3
Ball fall viscosity (secs.)	41	46
Xanthate sulfur, percent	1.20	0.94
Fiber properties, denier	1.4	1.4
Conditioned:		
Tenacity, g.p.d	5.0	4.3
Elongation, percent	9.3	9.3
Wet:		
Tenacity, g.p.d	3.8	3.4
Elongation, percent	9.8	8.8
Modulus at 5% extension g.p.d	1.2	1.0

These results, compared with those of Example VII, show that when the viscose modifiers, dimethyl amine and polyethylene glycol are omitted from the viscose, large reductions in physical properties occur. This is observed for conditioned, wet tenacities and wet moduli of the fibers produced.

In addition, properties of fiber of Example VIII produced from unmodified, ripened viscose show a larger degree of reduction as a result of ripening than those of fiber produced from the modified, ripened viscose of Example VII. In the latter case, fiber properties produced from unripened and ripened modified viscose were almost identical.

In the accompanying drawings:

FIG. 1 is a rectilinear diagram based on the proportions of formaldehyde and zinc sulfate illustrating in the shaded area the preferred and most advantageous proportions of these agents.

FIG. 2 is an exact reproduction of a group of rayon filaments produced in the process of Example I, Sample A. The filaments were cast in wax, cross-cut and subjected to differential dyeing for photographing under a magnification of 2200X.

FIG. 3 is a flow diagram illustrating a typical process of the invention.

As used herein, "conditioned tenacity" is the tenacity measured after the filaments have been maintained for 24 hours at a temperature of 75° F. at 50% relative humidity.

"We tenacity" is the tenacity of the filaments measured while totally immersed in water at a temperature of 20° C.

"Wet modulus" is the wet strength of filaments in grams per denier measured at 5% elongation.

The "gamma number" is the amount of xanthate groups substituted on the cellulose times 100.

What is claimed is:

1. The improved process for producing high tenacity rayon filaments having a conditioned tenacity of about 6 g.p.d., a wet modulus of about 1 to 2, a wet tenacity of about 3 to 5 g.p.d., an elongation of about 8 to 12%, and high flexibility which comprises

preparing a viscose spinning solution from cellulose xanthate having 450 to 800 D.P., said viscose solution being equilibrated to approximately the temperature of the coagulating bath into which the viscose solution is to be extruded, said viscose solution having a gamma number of about 40 to 90, a salt index of about 7.5 to 12 and containing a modifier which substantially retards regeneration,

extruding said viscose solution into the coagulating bath at a temperature of from 18 to 30° C., said bath containing from 3 to 9% by weight H_2SO_4, from 7 to 18% by weight of Na_2SO_4, from 0.2 to about 2% by weight formaldehyde, and from 1 to 6% by weight zinc sulfate,

stretching the resulting coagulated filaments from 110 to 250% in length, but at least 60% of the total stretch, prior to substantial regeneration, and

stretching of the filaments for at least an additional 30% in length, but not more than 40% of the total stretch or beyond filament damage, while the filaments are undergoing complete regeneration in contact with a regenerating liquid at a temperature of from 60° to 100° C.

2. The process according to claim 1 in which the viscose has a viscosity of 20–150 ball fall seconds and in which the viscose is modified by the addition thereto of regeneration retardants comprising dimethyl amine and polyethylene glycol.

3. The process according to claim 1 characterized in that the spin bath contains formaldehyde and zinc sulfate in the proportions shown in the shaded area of FIG. 1.

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JULIUS FROME, Primary Examiner

J. H. WOO, Assistant Examiner

U.S. Cl. X.R.

264—191

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,494,996 Dated February 10, 1970

Inventor(s) HUGH D. STEVENS, ROBERT B. KENNEDY, AND GEORGE C. DAUL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 27, "suitable" should read -- suitably --;

Column 2, line 42, "deareation" should read --deaeration --;

Column 3, line 44, "balanec" should read --balance--;

Column 5, line 70, "65%" should read -- 6.5% --;

Column 7, line 29, "two" should read -- tow --;

Column 7, line 37, "showing" should read -- shown --

Column 8, line 46, "We tenacity" should read --"Wet tenacity"--

SIGNED AND
SEALED
JUL 21 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents