

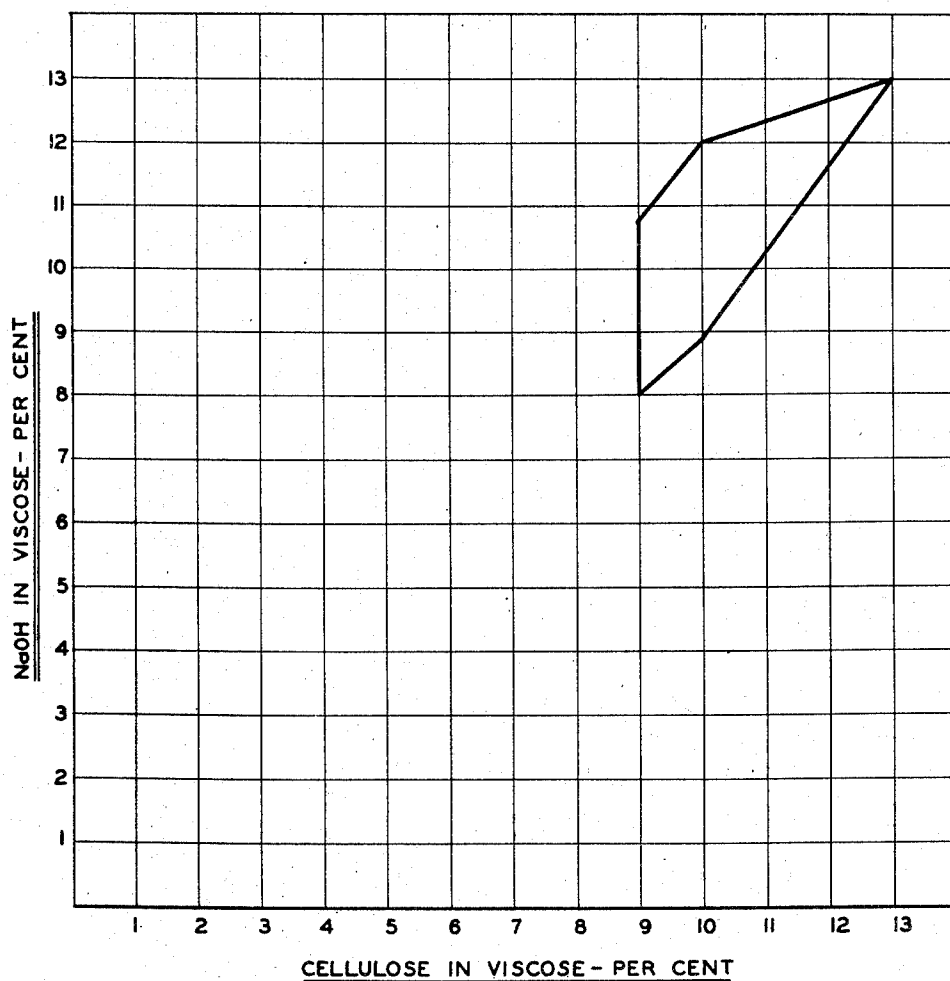
Dec. 20, 1949

P. H. SCHLOSSER ET AL

2,491,938

METHOD OF PRODUCING VISCOSE FILAMENTS

Filed Oct. 18, 1944



INVENTORS
PAUL HENRY SCHLOSSER
REID LOGAN MITCHELL
KENNETH RUSSELL GRAY

BY

Annis, Edmonds, Morton and Barrows
ATTORNEYS

UNITED STATES PATENT OFFICE

2,491,938

METHOD OF PRODUCING VISCOSE
FILAMENTS

Paul Henry Schlosser, Reid Logan Mitchell, and
Kenneth Russell Gray, Shelton, Wash., as-
signors to Rayonier Incorporated, Shelton,
Wash., a corporation of Delaware

Application October 18, 1944, Serial No. 559,234

9 Claims. (Cl. 18—54)

1

This invention relates to viscose production and has for its object the provision of an improved method of producing spun filaments and the like. More particularly, the invention provides an improved method of producing crinkled or potentially crinkled regenerated cellulosic filaments of viscose origin.

The method of the invention, in its broad aspects, is characterized by spinning a viscose solution into a coagulating and regenerating spin bath in which a slow regeneration is effected while the filaments are under low tension, regenerating completely while under low tension or in a relaxed state, and thereafter subjecting the filaments to high tension stretching while wet to develop such a condition in the filaments that the filaments crinkle spontaneously when wet with water under conditions permitting free shrinkage. The delayed stretching under high tension of the filaments which have undergone a slow or retarded regeneration results in a strained structure which causes them to crinkle.

The term "low tension," as used herein, applies to operations in which the newly formed filaments are drawn off under low tension as in a regular spinning operation, for example, under tensions of around 0.3 gram per denier or less. In other words, the filaments, during the operation of coagulation and regeneration (partial at least), are under only a sufficiently positive tension that they are drawn through the spin bath at a speed in excess of the extrusion speed.

The term "high tension" stretching, as used herein, refers to tensions above 0.5 gram per denier and especially to tensions of 0.75 to 1.0 gram per denier or higher, or in any case sufficient tension to exert a maximum degree of stretching on the completely regenerated filaments. Actually the upper limit in high tension stretching is the point where damage to the filaments is noticed, either through visible breakage, or as evidenced by sticking of filaments on either stationary or roller guides.

In one of the embodiments of the invention, we use a viscose of special composition and spin the filaments in a coagulating and regenerating spin bath under low tension, and, after complete regeneration, subject the filaments to high tension stretching. The resulting regenerated and stretched cellulosic filaments have the capacity to crinkle spontaneously when treated with water under conditions permitting free shrinkage. The special viscose solution used in a method of the invention is relatively high in both the cellulose and the caustic soda contents and is spun

2

in an acid spin bath wherein the tension during the operation of coagulation and regeneration is very low; preferably only sufficient tension is used to effect a positively controlled removal of the filaments from the spin bath. Coagulation and regeneration are preferably carried out with a normal Muller bath such as is commonly used with normal composition viscoses in spinning ordinary non-crinkled yarns.

The single figure of the accompanying drawing illustrates compositions of the invention graphically.

In carrying out our invention with viscose of special composition, we use a viscose solution having a cellulose content of from 9% to 13%, and a caustic soda content of from 8% to 13%, with a cellulose to caustic soda ratio of from 0.833 to 1.13. Under the most favorable conditions, a viscose containing about 10% each of cellulose and caustic soda gives the most effective crinkling. However, compositions close to this, such as 10 to 9, 10 to 11, 9 to 9, 9 to 10, and 11 to 11 of cellulose and caustic soda, respectively, give very effective and desirable crinkling under suitable spinning conditions. Graphically, the operative range of this invention may be expressed by the area encompassed by a pentagon bounded by the following points when located on the ordinate diagram of the drawings:

9% cellulose, 8% caustic soda
9% cellulose, 10.8% caustic soda
10% cellulose, 12% caustic soda
13% cellulose, 13% caustic soda
10% cellulose, 8.9% caustic soda

Under the preferred conditions as exemplified by a viscose having a cellulose content of 10% and a caustic soda content of 10%, the ratio of cellulose to caustic soda is 1.0. This also is the preferred ratio for any of the other cellulose values which have been found to be workable, namely, 9% to 13%. This preferred ratio of 1.0 becomes the more critical the more the value of 13% cellulose concentration is approached. In other words, the greatest leeway in the choice of the cellulose to caustic soda ratio within the restricted ratio range of 1.13 to 0.833 is afforded at cellulose concentrations of not over 10% where the whole range is effective. But as the extreme high cellulose concentration is 13% is approached, the ratio of caustic soda to cellulose narrows down to the preferred value of 1.0. The viscose may have a salt index varying from around 4.0 to 7.5, a preferred range being from 5.5 to 6.0, and especially when spinning a viscose contain-

ing about 10% each of cellulose and caustic soda.

In accordance with this aspect of the invention, a viscose solution of the special composition is extruded into or otherwise suitably contacted with a regenerating medium, for example, a normal Muller bath. A normal Muller bath, as referred to herein, is a spin bath in which sulfuric acid and sodium sulfate are present in such proportions that the bath consists substantially of a solution of NaHSO_4 together with some excess Na_2SO_4 . Such a bath may contain in addition MgSO_4 , glucose and ZnSO_4 , the latter in amounts up to about 1.5%. The term "normal Muller bath" does not refer to baths containing iron, manganese, chromium or other metals of that class in any appreciable quantity or zinc in amounts greater than 1.5%. Such special baths have a highly delayed regenerating action, and while sometimes used for spinning, nevertheless, are not of the character used in this embodiment of this invention employing a special viscose which has slow regenerating characteristics. The bath is preferably used at a temperature within the range of 45° C. to 55° C. However, some deviations from these upper and lower limits are permissible.

The filaments formed by extruding this special slow acting viscose into the normal Muller bath are drawn off under low tension as in a regular spinning operation on an ordinary spinning frame, and collected on one of the usual collecting devices. At this stage the filaments are normal in appearance and straight (and will stay straight if finished in a normal manner), but when they are stretched under high tension at a later time and then allowed to shrink freely, crinkling occurs immediately and spontaneously. The filaments may be stretched after-complete regeneration while in the acid condition but preferably after washing. They may even be stretched after washing, drying and rewetting. The high tension stretching and crinkling will be described more fully hereinafter.

In another embodiment of the invention we use a normal viscose solution but spin the viscose under low tension into a coagulating regenerating bath of special composition which is characterized by a relatively slow regenerating action. The filaments spun under low tension are removed from the spin bath and permitted to age for a period in an acid condition until regeneration is complete and are thereafter subjected to high tension stretching with the result that the filaments crinkle spontaneously when wet under conditions permitting free shrinkage. The delayed or continuing regeneration following the low tension spinning in the spin bath may be effected in any suitable manner, preferably by collecting the filaments on a bobbin or in a cake in a more or less slack condition while wet with adhering spin bath, washing in package form, and then subjecting them to the high tension stretching on a multiple end slasher.

In that embodiment of our invention in which we spin a normal viscose into a special spin bath under low tension, we effect a slow or delayed regeneration which is continued for a time beyond the spinning operation and before the high tension stretching. A salt index of about 4 is very suitable. By a normal viscose, we mean one containing from around 7% to 8.5% of cellulose and from around 6% to 7.4% of caustic soda, the ratio of cellulose to caustic soda being about 1.15. The special spin bath used in this adaptation of the invention is one which is characterized

by a slow regenerating action. Spin baths which we have found suitable for the method of our invention comprise compositions of about the following:

	Grams per liter
H_2SO_4 -----	90
Na_2SO_4 -----	300
ZnSO_4 -----	42
Specific gravity, 1.3.	

After the filaments are subjected to coagulation and preliminary regeneration under low tension spinning, they are left in a more or less relaxed state for a short time, for example, from 10 minutes to from 3 to 4 hours, under regenerating conditions. This continuing regeneration may be effected while the filaments are wound on bobbins, in cake form, or in skeins and in contact with a regenerating medium, preferably in contact with adhering spin bath. The filaments should not be left in contact with the spin bath longer than necessary and particularly to a point where the acid begins to cause a deterioration of the cellulose. The filaments, after completion of the delayed regeneration, are ready for the high tension stretching.

The regenerated filaments, whether produced from the special viscose in a normal spin bath or from normal viscose in a special spin bath as previously described, are subjected to a high degree of stretching in any appropriate manner, and at any convenient time, for example, while wet with the spin bath, or during or after washing, or during or after bleaching or even after drying and rewetting. The high tension stretching may be carried out as an operation entirely separate from the spinning operation, often conveniently during, or as a supplementary operation to, the finishing treatments. For example, an operation such as is used in the finishing of high tenacity tire cord yarn is very desirable. The filaments, if in cakes or on bobbins, may be stretched on a simple slasher, or, if in skeins, may be stretched in a skein stretcher at any convenient stage in the finishing operation (even after drying and rewetting) and then allowed to crinkle spontaneously under conditions permitting free and rapid shrinkage. In any event, to secure the highest degree of crinkling, the regenerated filaments should be stretched in a wet condition to just below their breaking point, placed in water, if not already in water, and allowed to shrink as quickly and as freely as possible.

Stretching of the filaments in water may be to the extent of 30% to 50% but in case of rewetted filaments can be advantageously increased through the use of certain aqueous swelling baths as, for example, 1% NaOH in water or 5% dibenzyl dimethyl ammonium hydroxide in water.

The conditions which must be observed in the practice of the invention are somewhat critical. Slight variations in viscose composition, in spin bath composition, in bath temperature, in spinning tension and filament denier all affect the crinkle. Satisfactory crinkling depends upon the maintenance of a particular state during coagulation and regeneration, upon the acquiring of a latent crinkling structure, and upon the applying of stress to that structure.

At the completion of the high tension stretching, the filaments may be prevented from crinkling either by drying them under tension or by chemically treating the wet yarn with a medium which inhibits crinkling. The result in

either case is a straight product having the capacity to crinkle when treated with water under conditions permitting free shrinkage.

The simplest method of producing straight filaments with a capacity to crinkle is to simply dry the washed filaments under tension; for example by stretching and drying on a slasher. Another desirable procedure may be to lead the highly stretched and washed filaments while under tension through a bath containing, for example, a saturated solution of ammonium sulfate. If the spin bath is washed out of the yarn directly with the ammonium sulfate solution instead of with water, tension is not needed. In any case the filaments are prevented from crinkling by the inhibiting action of the ammonium sulfate and can be cut, opened and dropped into water, thereby crinkling spontaneously, or may be preserved for long periods of time in the wet state as finished filaments having the capacity to crinkle.

A swelling bath, comprising, for example, 1% NaOH in water, or 5% dibenzyl dimethyl ammonium hydroxide in water, may be particularly useful in reswelling dried filaments for purposes of crinkling.

Treatment of the stretched and straight filaments with water as by washing, dipping, spraying, or the like causes the strains in the stretched filaments to assert themselves and to crinkle the filaments when under conditions permitting free shrinkage. Wet filaments, stretched while still wet with spin bath, are usually not under conditions permitting free shrinkage due to the presence of substantial amounts of inhibiting electrolytes, such as sodium sulfate from the spinning solution. Treatment of such filaments with water reduces the concentration of the electrolyte, and in the absence of a mechanical restraining force, the filaments will crinkle. In the case of filaments washed and dried while restrained from shrinkage by mechanical force, treatment of the dry filaments with water, as by simple immersion, under conditions permitting free shrinkage, namely, in the absence of any restraining mechanical force on the filaments, causes the filaments to crinkle. Such shrinkage with water may be effected with fresh water or with any suitable water solution providing the water does not contain a high concentration of a material that inhibits crinkling such as ammonium sulfate, sodium sulfate, or potassium fluoride. Only strong solutions of these salts exert sufficient lyotropic action to prevent crinkling—even a 10% solution still allows good crinkling.

On the other hand as previously described, the water may contain materials which aid crinkling—as for example, small concentrations of NaOH or dibenzyl dimethyl ammonium hydroxide or a high concentration of KI or KCNS.

The following are illustrative examples of the invention:

Example I

Viscose with a composition of 10% cellulose, 10% NaOH and viscosity of 50 sec. (falling ball) was spun at a salt index of 5.8 into a common spin bath (140 g./liter H_2SO_4 , 245 g./liter Na_2SO_4 , 50 g./liter glucose, 12.5 g./liter $ZnSO_4$) maintained at 47° C. using 100-hole spinneret having holes 0.0020 of an inch in diameter. The collected filaments of 150 total denier were drawn out of the spin bath at a speed of 85 meters per minute and under a tension of about 20 grams (less than .2 g./denier) and collected on a bobbin. The

bobbin of yarn was washed acid-free then put on a slasher, stretched 30% and dried under tension. The dried yarn was skeined then immersed in a hot water desulfuring bath containing about 1% NaOH; crinkling occurred immediately. The skeins were then bleached, oiled and dried. The filaments were highly crinkled, of dull lustre and skeins were bulky and of good hand. The tenacity was 2.3 g./denier dry, 1.3 g./denier wet; elongation (with crinkles straightened out) equalled 20% when dry and 30% when wet. The additional elongation due to crinkle was about 25%.

If the yarn is collected in a centrifugal pot with a twist of 3 to 4 turns per inch, free shrinkage is somewhat restricted by the twist, but a bulky yarn is nevertheless obtained which shows a distinct spiral structure overlying the finer individual crinkles.

Example II

Viscose made from wood pulp and having the composition of 10% cellulose and 10% sodium hydroxide at a sodium chloride index of 5.3 was spun into an acid spin bath with composition 125 g./liter H_2SO_4 , 235 g./liter Na_2SO_4 , 12.5 g./liter $ZnSO_4$ maintained at a temperature of 47.5° C. The viscose was extruded from a spinneret having 480 holes, each hole being 0.0030 inch in diameter at a rate to give filaments of 1100 total denier which were then drawn through the coagulating and regenerating bath for a distance of 100 inches under a spinning tension of 200 grams and then wound up on a bobbin at a speed of 85 meters/minute. Several bobbins of yarn were washed acid free and then on a simple slasher the collected ends were stretched 30% and led through a bath containing 50% $(NH_4)_2SO_4$ solution, excess solution being removed with squeeze roll. The bundle of filaments was then cut to 4-inch staples, opened and dropped into a large volume of water, thereby crinkling immediately and spontaneously. The 4-inch staple chips were only 1 inch in length after shrinkage; the takeup being largely due to development of crinkle. Each crinkled chip was very bulky and springy and could readily be drawn out into an elongated sliver merely by pulling with the fingers. Crinkles numbered about 25 to the inch and had an amplitude of about $\frac{1}{2}$ inch. Tensile tests on the single fiber gave a tenacity of from 2.5 to 3.0 g./denier.

Example III

Viscose with a composition of 9% cellulose and 8% caustic soda, a viscosity of 60 seconds falling ball and a salt index of 5.4 was spun into a spin bath with a composition of 145 g./liter H_2SO_4 , 330 g./liter Na_2SO_4 , 13 g./liter $ZnSO_4$ and 55 g./liter glucose at 50° C. using a spinneret with 480 holes, each having a diameter of .0030 of an inch. The filaments of 1100 total denier were grouped into a thread which was drawn from the coagulating and regenerating bath for a distance of 100 inches under a tension of 200 grams at a speed of 85 meters per minute and collected on a bobbin. Staples cut from the bobbin at this stage and dropped into water showed no tendency to crinkle. However, when the yarn was stretched to just below the breaking point on two sets of rollers traveling at different speeds, then cut and dropped into water a fine crinkle developed immediately. It is important to subject the filaments to high stretch since the higher the stretch the finer and more frequent the crinkles.

If, in the above example, a viscose with the composition 7% cellulose and 6% caustic soda is used and the yarn subjected to the same spinning and stretching conditions no significant crinkling is obtained. If, on the other hand, a viscose with 10% each of cellulose and caustic soda is used, crinkle is somewhat finer than for a viscose with 9% cellulose and 8% caustic soda.

Example IV

Viscose with a composition of 7.5% cellulose, 6.5% NaOH and viscosity of 35 sec. (falling ball) was spun at a salt index of 4.0 into a spin bath having a composition of 90 g./liter H_2SO_4 , 300 g./liter Na_2SO_4 , 42 g./liter ZnSO_4 maintained at 47° C. using a 60-hole spinneret having holes 0.0031 of an inch in diameter. The collected filaments of 150 total denier were drawn vertically out of the spin bath after an immersion of 15 inches at a speed of 85 meters per minute and under a tension of about 20 grams (less than 0.2 g./denier) and collected on a bobbin. The yarn was washed acid free on the bobbin, skined while wet, stretched 30% and relaxed in water whereupon crinkling occurred immediately.

The crinkled skeins were then bleached, oiled and dried. The filaments were highly crinkled, of dull lustre and the skeins were bulky and of good hand.

In accordance with the invention, filaments have been produced which show a wide variety of three-dimensional crinkle, both in filament yarn and in staple. The process is particularly adapted to spinning of fool-like staple fiber having filament deniers of 1-7 or even lower. The ability to spin crinkled filaments of such fine denier is particularly notable. Yarn of, for example, 2 denier per filament is exceptionally soft, has an exceedingly large number of crinkles per inch and has very good tensile properties. Tensile tests on single staple fiber show tenacities of greater than 3 g./denier dry with elongations of about 20% in the fiber itself not considering the elongation due to crinkle. The elongation due to crinkle in these staples is often greater than 100%.

From the preceding results and characteristics, it appears that the tendency to crinkle is an inherent characteristic of the filaments of the invention and after having once been stretched and relaxed the crinkled form represents the normal equilibrium state.

When the straight dry yarn (washed, stretched and dried under tension) is treated with water while free to shrink, it is usually found that the crinkling incurred is somewhat less than the crinkling effect obtained with similar yarn which has been treated with water and allowed to shrink immediately after being taken from the stretching machine. In other words, washing and drying under tension tends to reduce somewhat the degree of crinkling. It has, however, been found that with this dried yarn, certain solutions such as a 50% aqueous solution of potassium iodide, a 1% solution of NaOH, or a 5% solution of dibenzyl dimethyl ammonium hydroxide return the yarn to a highly swollen gel state and give better crinkling than does water alone; no better, however, than is originally obtained if crinkling has been induced with water before the yarn has been dried at all.

Filaments preserved in the straight state with a substantially saturated solution of ammonium sulfate are not subject to marked deterioration and may be kept in the straight form, then con-

verted at will into the crinkled form merely by washing with water. Apparently, acid alone over a wide range in concentration has little, if any, effect on crinkling of the filament but will, of course, over a period of time if left in the filament, exert some degrading influence on the cellulose itself.

The different performance of the above-given examples of ammonium sulfate and potassium iodide when added in high concentrations to the wash water may possibly be explained by the progressive influence of the anions as exemplified in the well-known Hofmeister series registering the order of lyotropic action of ions. In this series the sulfate ion is near one extreme, whereas the iodide ion is near the other.

An experiment illustrating the permanency of the crinkles may be carried out by simply boiling some of the crinkled filaments in water for a period of several hours, then drying. Repeated treatments of this sort do not noticeably impair the crinkles. It is notable that the crinkles are so permanent in the wet state.

When a sample of crinkled filaments is dropped into a caustic soda solution of about 6% concentration, swelling is great and the crinkles disappear leaving the filaments essentially straight. If, however, the filaments are removed from the caustic soda, washed with water free of caustic soda, and dried, it is found that the crinkles have been regained and to a degree comparable to the original. If a caustic soda solution of 18% concentration is used instead of 6%, the swelling is less and the crinkles do not completely disappear from the filaments while immersed in the caustic soda solution.

An important advantage of our invention is the providing of a simple, effective method for spinning crinkled or potentially crinkled viscose filaments on the conventional single bath type spinning frame commonly used for the spinning of non-crinkled yarns or non-crinkled staple fiber tow. For example, one type of single bath spinning operation to which the invention is particularly suited is carried out on a conventional viscose spinning apparatus which is not equipped with any stretching device whatsoever or in any case devices for applying high stretch. Such latter type of apparatus is commonly used for spinning of regular tenacity non-crinkled yarn at relatively low stretch. It is to be emphasized that the invention provides a method for spinning crinkled filaments in a single bath spinning operation without requiring any mechanical alterations from the apparatus normally used for spinning straight filaments.

The invention also obviously provides for a flexible method for changing a viscose rayon operation back and forth between production of crinkled and straight filaments without the necessity for mechanical alterations on the spinning frames.

We claim:

1. The improvement in the viscose process which comprises forming a viscose solution having about 10% each of cellulose and caustic soda, extruding the viscose into an aqueous acid spin bath to form cellulose filaments, said spin bath comprising about 125 to 145 grams per liter of sulfuric acid and 235 to 330 grams per liter of sodium sulfate in such proportions that the bath consists substantially of NaHSO_4 with some excess Na_2SO_4 and around 12.5 grams per liter of zinc sulfate, coagulating and regenerating the fila-

ments under a tension of less than 0.3 gram per denier, and then after regeneration is complete, subjecting the filaments to high tension stretching under a tension of at least 0.5 gram per denier while wet, whereby the filaments acquire the potential capacity to crinkle spontaneously when treated with water under conditions permitting free shrinkage.

2. The improvement in the viscose process which comprises forming a viscose solution having about 10% each of cellulose and caustic soda, extruding the viscose into an aqueous sulfuric acid spin bath comprising about 125 to 145 grams per liter H_2SO_4 , 235 to 330 grams per liter Na_2SO_4 , and around 12.5 grams per liter $ZnSO_4$ to form cellulose filaments and during the operation of coagulation and regeneration drawing the filaments from the spin bath under a tension of less than 0.3 gram per denier and then after regeneration is complete subjecting the filaments to high tension stretching under a tension of at least 0.5 gram per denier while wet, whereby the filaments acquire the potential capacity to crinkle spontaneously when treated with water, and crinkling the filaments in water containing a swelling agent.

3. The improvement in the viscose process which comprises forming a viscose solution having from 9% to 13% of cellulose and from 8% to 13% of caustic soda, the ratio of cellulose to caustic soda being from 0.833 to 1.13, extruding the cellulose into an aqueous sulfuric acid spin bath comprising about 125 to 145 grams per liter H_2SO_4 , 235 to 330 grams per liter Na_2SO_4 , and 12.5 grams per liter $ZnSO_4$ resulting in a relatively slow regeneration to form cellulose filaments, during the operation of coagulation and regeneration subjecting the filaments to a tension of less than 0.3 gram per denier, sufficient only to effect a positive withdrawal from the spin bath, and then subjecting the completely regenerated filaments to stretching under a tension of more than 0.5 gram per denier while wet, whereby the stretched filaments develop the capacity to crinkle spontaneously on wetting with water while free to shrink.

4. The improvement in the viscose process which comprises extruding a viscose solution into a coagulating and regenerating aqueous acid spin bath, drawing the resultant filaments from the spin bath at a rate at least equal to the extrusion rate under a tension not over 0.3 gram per denier to form straight cellulose filaments, removing the filaments from the spin bath and collecting them, leaving the collected filaments to relax and to relieve tension thereon while in contact with adhering spin bath for at least ten minutes, said spin bath being of such composition in relation to the amount of cellulose and caustic soda in the viscose that regeneration is completed while the relaxed filaments are in contact with the spin bath, and after regeneration is complete subjecting the straight filaments while wet to high tension stretching under a tension of more than 0.5 gram per denier, whereby the filaments develop the capacity to crinkle.

5. The improvement in the viscose process de-

fined in claim 4 in which the viscose solution contains from 7% to 8.5% of cellulose and from 6% to 7.4% of caustic soda, the spin bath comprises approximately 90 grams per liter sulfuric acid, 300 grams per liter sodium sulfate and 42 grams per liter zinc sulfate, and after the high tension stretching the filaments are wet with water containing a swelling agent to cause crinkling of them.

6. The improvement in the viscose process defined in claim 4 in which the viscose solution contains from 7% to 8.5% of cellulose and from 6% to 7.4% of caustic soda, the spin bath comprises approximately 90 grams per liter sulfuric acid, 300 grams per liter sodium sulfate and 42 grams per liter zinc sulfate, in which the filaments are dried after the high tension stretching while they are prevented from shrinking or crinkling, and in which the filaments thereafter are wet with water containing a swelling agent to cause crinkling of them.

7. The improvement in the viscose process defined in claim 4 in which the viscose solution contains from 7% to 8.5% of cellulose and from 6% to 7.4% of caustic soda.

8. The improvement in the viscose process defined in claim 4 in which the viscose solution contains about 7% cellulose and about 6% caustic soda, and the spin bath comprises approximately 90 grams per liter sulfuric acid, 300 grams per liter sodium sulfate, and 42 grams per liter zinc sulfate and has a specific gravity of about 1.3.

9. The improvement in the viscose process defined in claim 4 in which the viscose solution contains from 7% to 8% cellulose and from 6% to 7.4% caustic soda, and the spin bath comprises approximately 90 grams per liter sulfuric acid, 300 grams per liter sodium sulfate, and 42 grams per liter zinc sulfate and has a specific gravity of about 1.3.

PAUL HENRY SCHLOSSER.
REID LOGAN MITCHELL.
KENNETH RUSSELL GRAY.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,015,201	Stockly et al. -----	Sept. 24, 1935
2,233,418	Kline et al. -----	Mar. 4, 1941
2,249,745	Charch et al. -----	July 22, 1941
2,267,055	Tippetts -----	Dec. 23, 1941
2,287,839	Stoeckly -----	June 30, 1942
2,297,613	Fink et al. -----	Sept. 29, 1942
2,297,746	Charch et al. -----	Oct. 6, 1942
2,312,152	Davis -----	Feb. 23, 1943
2,315,560	Stoeckly et al. -----	Apr. 6, 1943
2,340,377	Graumann et al. -----	Feb. 1, 1944
2,347,883	Cox -----	May 2, 1944
2,347,884	Cox -----	May 2, 1944

FOREIGN PATENTS

Number	Country	Date
462,184	Great Britain -----	Mar. 4, 1937
483,404	Great Britain -----	Apr. 20, 1938
492,279	Germany -----	Sept. 19, 1922