July 18, 1950 W. D. NICOLL 2,515,834

CELLULOSE FILAMENTS AND METHOD OF PRODUCING SAME

Filed Nov. 13, 1942 2 Sheets-Sheet 1

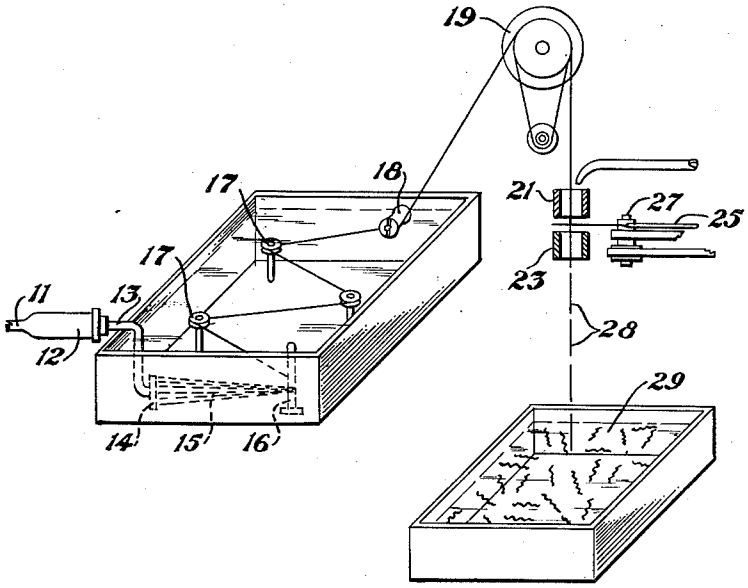


Fig. 1

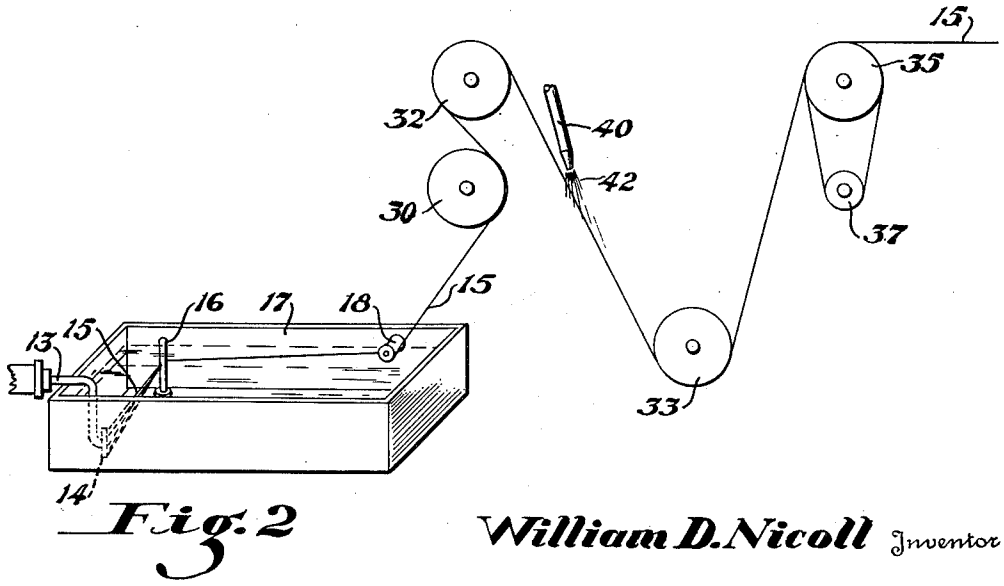


Fig. 2

William D. Nicoll Inventor

By Louis White

Attorney

July 18, 1950 W. D. NICOLL 2,515,834

CELLULOSE FILAMENTS AND METHOD OF PRODUCING SAME

Filed Nov. 13, 1942 2 Sheets-Sheet 2

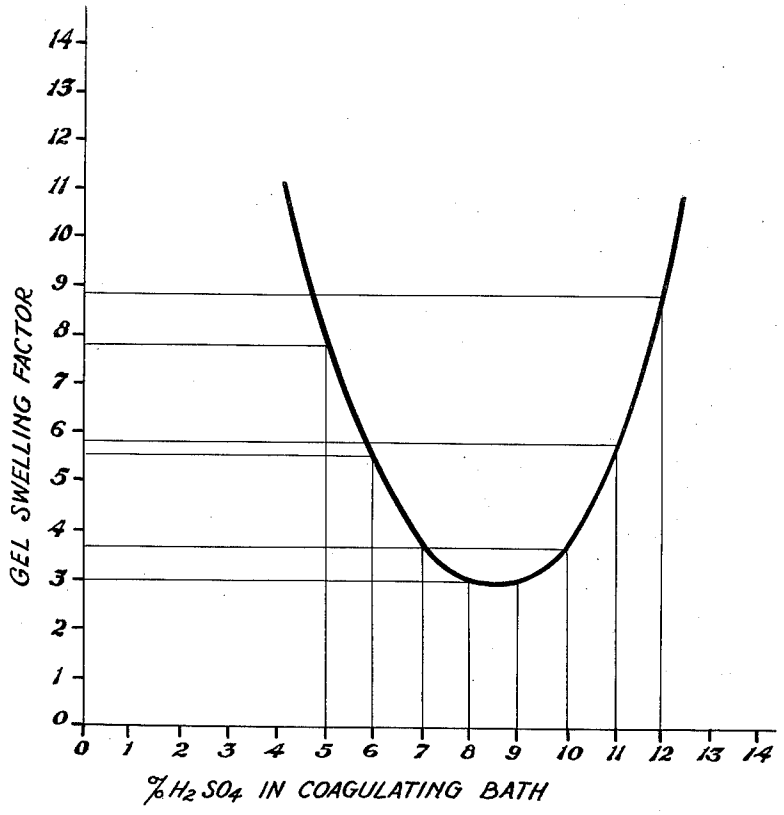


Fig. 3

William D. Nicoll Inventor

By Louis a. White

Attorney

Patented July 18, 1950 2,515,834

UNITED STATES PATENT OFFICE

2,515,834

CELLULOSE FILAMENTS AND METHOD OF PRODUCING SAME

William D. Nicoll, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application November 13, 1942, Serial No. 465,414

43 Claims. (Cl. 28—82)

1

This invention relates to the production of new and unique crimped, wool-like, regenerated cellulose filaments and fibers, and a new and improved process for obtaining such products.

This application is a continuation-in-part of my copending applications Serial No. 318,326 and Serial No. 318,327 filed February 10, 1940, both now abandoned.

It is an object of the present invention to produce, from viscose, highly crimped fibers and filaments of regenerated cellulose which are characterized by high tensile strength.

It is another object of this invention to produce, from viscose, crimped, wool-like fibers and filaments of regenerated cellulose which are entirely new and unique in character in that the crimp, after being removed mechanically, for example by stretching, combing, or the like, may be substantially completely restored by suspending the same, free from all tension, in an aqueous liquid.

It is another object of the present invention to provide a new and improved process for the spinning of regenerated cellulose filaments and fibers from viscose solutions and subjecting said filaments and fibers to a relaxing treatment whereby to impart an intense crimp to said filaments and fibers, which process comprises the substantially complete regeneration of the filaments or fibers prior to the relaxing treatment thereof.

Other objects of the invention will appear hereinafter.

It is well known that the viscose process for spinning regenerated cellulose filaments is a highly critical process. Comparatively slight variations in the composition of the viscose or in the composition of the spinning bath will prevent satisfactory spinning. This is clearly evidenced by the fact that in commercially useful processes, the art has found it imperative to stay within narrow limits with respect to the cellulose and alkali contents of the viscose and the constituents of the spinning bath.

One of the most important considerations in the critical balance between viscose composition and the composition of the spinning bath is what will here be called the "gel swelling factor." To constitute a commercially useful viscose rayon process, the viscose composition and the sulfuric acid coagulating bath composition employed must be so balanced as to permit the production of regenerated cellulose filaments having a gel swelling factor of 6.5 or less and in most instances actual commercial spinning processes will employ conditions which yield filaments exhibiting a gel

2

swelling factor which is less than 6.5. The gel swelling factor of regenerated cellulose filaments is determined in the following manner:

A viscose of known composition is extruded through a spinneret into a sulfuric acid coagulating bath of known composition. The coagulated filaments, after leaving the bath, are wound in a single layer on to a bobbin with a helical wind of narrow pitch in such a manner that successive windings are very closely spaced. When the bobbin contains 2 to 6 grams of wet gel yarn, the bobbin is removed and rotated on a chuck to centrifuge off the bath carried with the filaments on to the bobbin. The acid-wet gel yarn is then cut from the bobbin and weighed. The whole operation should be carried out within four minutes. The acid-wet gel yarn is washed and then dried to remove all the water therefrom and the dry yarn reweighed. The ratio of the weight of acid-wet gel yarn to the weight of the dry yarn is termed its "gel swelling factor."

It is possible for this gel swelling factor to range from about 3 to about 12, depending upon the composition of the viscose and of the coagulating bath. For a given viscose composition, a high concentration of sulfuric acid in the coagulating bath will result in the production of a regenerated cellulose having a high gel swelling factor. If the acidity is gradually decreased (with the composition of the viscose and coagulating bath otherwise remaining the same) the gel swelling factor falls to a minimum and then rises again with a further decrease in the acidity. The gel swelling factor at the minimum will be termed the "minimum gel swelling factor," and the acidity at this point will be termed the "minimum gel swelling factor acidity."

Heretofore the art has arrived at spinning conditions by empirical, trial and error methods. It is now recognized that the minimum gel swelling factor and the minimum gel swelling factor acidity actually play important roles in defining spinning condition. Thus, for example, for a given viscose, yarn properties such as tenacity, elongation, softness, etc., are, as a rule, best when spinning is done at or near the point of minimum gel swelling. In accordance with the present invention, in order to produce high strength, unique, intensely crimped regenerated cellulose filaments departure must be made from conventional spinning conditions. The definition and establishment of the new conditions required for the practice of this invention constitutes essential elements in the provision of a new spinning process and the products resulting therefrom.

Viscose-sulfuric acid-salt systems in which the minimum gel swelling factor of the regenerated cellulose filaments obtainable therefrom is less than 6.5 will hereinafter be referred to as balanced viscose-sulfuric acid-salt spinning bath systems."

It has now been discovered that high strength, unique, intensely crimped regenerated cellulose filaments can be produced by observing the following highly critical combination of conditions: Spinning filaments in a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains zinc sulfate and the sulfuric acid content of the bath is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right]\cdot x$$

wherein

A is the percentage content by weight of sulfuric acid in the spinning bath,

K is a factor which may have any value from 1.9 to 2.5,

C is the percentage content by weight of cellulose in the viscose,

N is the percentage content by weight of caustic alkali (calculated as sodium hydroxide) in the viscose,

x is the percentage content by weight of sulfuric acid in the coagulating bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N;

imposing on said filament during the spinning thereof a tension of at least 0.5 gram per denier and a stretch of at least 40%; and, after substantially complete regeneration of said filaments, relaxing the same completely free of all tension in a liquid which will swell the same. [By "stretch of at least 40%" is meant a stretch (as measured between the point where the spun filaments are first converged in the bath, and collecting device) of at least 40% based on its unstretched length.] For practical purposes, it is generally desirable that the coagulating bath have a temperature of between 40° C. and 75° C. and preferably that the zinc sulfate content of the bath be from 0.1% to 3%.

The present invention may be more readily understood by reference to the following detailed description when taken in connection with the accompanying illustrations, in which:

Figure 1 is a diagrammatic side elevational view, with parts shown in perspective, of one embodiment of apparatus suitable for use in accordance with the invention;

Figure 2 is a similar diagrammatic view showing another embodiment of apparatus for use in accordance with the invention;

Figure 3 is a typical gel swelling factor curve.

Referring to Figure 1 of the drawings, reference numeral **11** designates a conduit line for a viscose filament-forming composition which is connected to any suitable source of supply, the conduit **11** is connected to a candle filter **12** and the candle filter **12** is connected to a spinneret **14** by means of "gooseneck" **13**. The viscose solution is extruded through the spinneret **14** to form filaments **15**. A bundle of filaments is passed over the fixed convergence guide **16**, and thence about roller guides **17** and take-off guide **18**. From guide **18**, the yarn is passed about feedwheel **19** which feeds the yarn through two vertically spaced sleeve guides **21** and **23**. If desired, a liquid may be passed through the two sleeve guides,

thereby to continuously force the yarn through said guides. A rotatable cutter knife **25** may be positioned rotatably between the two sleeve guides **21** and **23**, thereby cutting the yarn into small staple lengths. The cutter knife is mounted on a stub shaft **27** and is adapted to be rotated by means of a driven belt, as shown. The staple fibers **28** drop into a relaxing fluid **29** where they are completely free from all tension and will be quickly crimped along the length thereof.

Referring to Figure 2 of the drawings, the yarn **15** composed of freshly spun filaments is passed from the spinneret **14** about fixed convergence guide **16**, then through a long bath tank **17** to a take-off guide **18**. The yarn is then passed about draw-off rollers **30** and **32** which are of sufficient size to provide a surface area of sufficient extent to eliminate any material slippage of the yarn. The yarn is then passed from draw-off roller **32** about guide roller **33** and then about stretching rollers **35** and **37**. The yarn passes about rollers **35** and **37** a number of times to eliminate any possibility of slippage of the yarn. Between draw-off roller **32** and guide roller **33**, the yarn is subjected to treatment with a stretching bath **42**, passed on to the yarn by means of conduit **40**. The stretching bath will be described with particularity hereinafter. The draw-off rollers and stretching rollers are positively driven to impart a portion of the tension and stretch on the yarn between the guide **16** and the roller **30**, and a portion between the roller **30** and the roller **35**.

The apparatus shown in Figure 2 is particularly useful in such instances where the requisite tension and stretch cannot be imposed on the filaments solely in their travel through the spinning bath. It has been found that when such filaments are passed into contact with a stretching bath, the requisite tension and stretch can be imposed on the yarn during the spinning thereof.

Figure 3 of the drawings discloses a typical gel swelling factor curve for a viscose of a given composition. From this curve, it will be noted that when the acidity of the bath in per cent by weight of sulfuric acid is 12%, the gel swelling factor of the yarn will be slightly under 9.0. When the acidity of the bath is reduced to 11%, the gel swelling factor lies between 5.0 and 6.0. When the acidity is further reduced to 10%, the gel swelling factor drops between 3.0 and 4.0. With an acidity between 8% and 9%, the gel swelling factor has dropped to a minimum value of 3.0. Further reduction in the acidity of the coagulation bath will cause the gel swelling factor of the yarn to rise again in accordance with the contour of the curve shown in the drawing.

In its broad scope the process of the present invention is operative and useful with any balanced viscose-sulfuric acid-salt spinning bath system. A number of specific, detailed processes have been operated to good effect.

By way of illustration there will now be discussed three subgeneric embodiments of the broad concept which describe conditions particularly applicable when filaments are to be spun from the more common commercial viscose compositions. The first one has reference to the spinning of viscose having an alkali content of at least 5%, with or without the use of a secondary stretching bath. The second is concerned with systems using viscose of less than 5% alkali content in which a secondary stretching bath is used following the initial, substantially complete, coagulation and regeneration in a primary sulfuric

acid-salt bath. The third is concerned also with the use of viscose having less than 5% alkali, and spun in a single coagulating and regenerating bath, said viscose being modified by addition of a small amount of a salt of an amphoteric metal.

In accordance with the first subgeneric process of the present invention in which the viscose contains at least 5% alkali, the unique, crimped regenerated cellulose filaments may be obtained by observing the following relationship factors:

1. The viscose composition must have a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 1.5 and 6.
2. The coagulating and regenerating bath must have a sulfuric acid content of between 6.5% and 9.5%.
3. The coagulating and regenerating bath must have a sodium sulfate content of between 15% and 30%.
4. The coagulating and regenerating bath must have a zinc sulfate content of between 0.1% and 3%.
5. The filaments must travel at least 50 inches in the coagulating and regenerating bath.
6. The temperature of the coagulating and regenerating bath must be between 40° C. and 75° C.
7. The temperature of the relaxing bath must be between 20° C. and 120° C.
8. Imposing on the filaments, during the spinning thereof, a tension of at least 0.5 gram per denier and a stretch of at least 40%, and after substantially complete regeneration of the filaments, relaxing the same completely free of all tension in a liquid which will swell the same.

In addition to the above-mentioned ingredients of the coagulating bath, it is permissible to have present as much as 6% or 7% glucose or similar organic substances well known in the art. The presence of glucose in the spinning bath is not an essential feature of this process, but may be desirable, particularly when continuous filament yarn is produced. As a guide to the proportion of glucose used, it may be said that 2% of glucose can replace approximately 1% of sodium sulfate.

In accordance with the above detailed process the specifically enumerated factors are all interdependent and must be adjusted in relation to one another in order to obtain the desired result, i. e., a satisfactory crimp.

It is, of course, understood that relaxing of the filaments in an aqueous medium completely free of all tension is absolutely essential, no matter what variations may be introduced in the other conditions. It is also essential that the tension on the filaments during the spinning (including stretching) be at least 0.5 gram per denier, and that a stretch of at least 40% be placed on the filaments. For each of the factors enumerated above, the range within which the process may be successfully operated has been indicated but it will be apparent at once, to one skilled in the art, that, if any one of the factors is set at or near the extreme lower or upper limit of its particular range, other factors may have to be adjusted in order to obtain the best results. To illustrate, if the acid content of the coagulating bath is 6.5% (the lowest limit of the range), it is desirable to adjust some of the other factors to restore the balance of the conditions; i. e., in the case illustrated, neither the sodium sulfate nor the zinc sulfate contents of the coagulating bath can be the lowest permissible but are preferably increased to, for example, 19% and 2.5% respectively, and likewise the bath temperature should be raised to about 55° C.

For all the important variables, the range within which the process is operable has been indicated above. In view of the present detailed disclosure anyone skilled in the art will readily be able to adjust the conditions in relationship to one another so as to obtain excellent results.

For the purpose of making this process more readily understandable, the following table will be useful to show both the operable ranges and the "median" ranges. The median ranges comprise those ranges within which any one factor can be varied at will without necessitating a change in the other factors.

	Operable Range	Median Range
Alkali content of viscose	Over 5%	5.75–6.25%.
Salt index of viscose	1.5–6	3.5–5.5.
Acid content of the bath	6.5–9.5%	7.5–8.5%.
Sodium sulfate in the bath	15–30%	19–25%.
Zinc sulfate in the bath	0.1–3%	0.85–2.0%.
Length of bath travel	Over 50 inches	Over 75 inches.
Spinning tension	Over 0.5 g. p. d.	Over 0.5 g. p. d.
Temperature of coagulating bath.	40–75° C	50–60° C.
Temperature of relaxing bath	20–120° C	60–100° C.

Although no definite rules can be given for making all necessary adjustments permitting one to use conditions outside the median ranges but still within the operable range, it can be said, in general, that except for the alkali content of the viscose, the selection of one relationship factor outside the median range requires that all other factors be within this range. In the case of a change in the alkali content of the viscose, I have found that the most important other variable requiring adjustment is the acid content of the coagulating and regenerating bath. This can be done readily by using the general formula

$$A=\left[\frac{K(C.N)}{100}\right].x$$

discussed above. I have found as an empirical rule that, over the operable ranges shown, a 1% increase in alkali content of the viscose is approximately compensated for by a 1½% increase in the acid content of the coagulating and regenerating bath.

As above stated, it is essential in accordance with this invention that a tension of at least 0.5 gram per denier and a stretch of at least 40% be imposed on the filaments during the spinning thereof. The tension and stretch imposed on the filaments may, of course, greatly exceed that above specified. Any tension or stretch under that which will break the filaments may be used in accordance with the present invention. This tension and stretch must be imposed on the filaments during the coagulation and regeneration thereof when operating without a stretching bath as shown diagrammatically in Figure 1 of the drawings. In some instances, however, it may be impossible to impose that amount of stretch and tension without the use of a stretching bath. Under such circumstances, an arrangement as shown in Figure 2 of the drawings may be used. In the latter case, the requisite stretch and tension are partially imposed on the filaments during their passage through the coagulation and regeneration both and partially imposed thereon during their passage through the stretching bath.

The path of the filaments through the coagulating and regenerating bath liquor must be sufficiently long to substantially complete the regeneration thereof while in said bath. However, if the stretching bath is capable of regeneration due to heat or content of acid, the regeneration of the filaments may be completed in this bath. For the purposes of the present specification and claims the spinning of the filaments shall include the passage of the filaments through the stretching bath if a stretching bath is employed.

When a stretching bath is used in accordance with the present invention, it must follow the coagulating bath and the yarn must be passed through the same with a continuation of tension and stretching begun in the coagulating bath. The degree to which the filaments are stretched or tensioned in the coagulating bath may be approximately the same as the degree to which they are stretched or tensioned in the stretching bath. Under some circumstances, it may be desirable to stretch and tension the filaments to a greater degree in the coagulating bath than in the stretching bath. Under other circumstances, it may be desirable to impose a greater degree of stretch and tension on the filaments in the stretching bath than in the coagulating bath. The stretching bath should preferably have a temperature of between about 50° C. and the boiling point thereof. The stretching bath should be composed of a non-alkaline, aqueous liquid preferably containing not to exceed that acidity equivalent to 3% sulfuric acid. This bath is preferably composed of water.

The relaxing bath may be composed of any liquid which is capable of swelling the cellulose filaments. Since the filaments will be substantially regenerated by the time they are subjected to relaxation in the relaxing bath, the latter will have substantially no regenerating action on the filaments. The relaxing bath preferably comprises water and it may be acidic, neutral, or alkaline. The relaxing bath may contain an acid or a salt such as calcium chloride, sodium thiocyanate, calcium thiocyanate or the like. Such salts will often impart a particularly desired swelling action to the filaments whereby crimping takes place in a particularly desirable manner. Such relaxing baths may also contain purification agents such as sodium carbonate, caustic soda and the like, which may, similarly to the above-mentioned salts, also have a desirable swelling action on the filaments. A particularly desirable relaxing bath comprises 3.5% aqueous solution of caustic soda. The temperature of the relaxing bath may vary widely as this is not critical. Particularly good results, however, are obtained with a 3.5% caustic soda relaxing bath having a temperature of about 35° C. The relaxing bath may comprise or consist of organic liquids such as glycerol if the latter is used at a temperature of the order of 120° C., at which temperature glycerol is found to swell regenerated cellulose filaments. Regenerated cellulose filaments may be relaxed in a bath consisting of anhydrous liquid ammonia since the latter is capable of swelling cellulose. Whatever the composition and temperature of the relaxing bath may be, the filaments must be allowed to rest in the relaxing bath free of all tension so that they may swell as completely as possible in the liquid medium. The greater the swelling action on the filaments during relaxation, the more desirable the relaxing bath. The filaments may be passed directly to the relaxing bath from the stretching bath in the form of continuous filaments or staple fibers. Alternatively, the filaments passing from the stretching bath may be collected in any desired manner, for example on a bobbin in accordance with the bobbin spinning process, in a bucket cake in accordance with the bucket spinning process, or loosely in a container therefor. The product may be washed acid free, desulfured and/or bleached prior to the time it is immersed in the relaxing bath or it may be relaxed while in the acid state and then washed, desulfured and/or bleached after crimping has been accomplished. If the product is crimped before the acid is removed, hot water must be used as a relaxing agent and such agents as 3.5% caustic cannot be used. However, if the acid is removed before crimping, then either hot water or a caustic relaxing bath may be used.

As above set forth, it is essential that the filaments be completely relaxed so that they are free to shrink to the maximum extent. Probably the best method of securing such complete relaxation is to immerse the skeins or staple in the relaxing bath, making sure that there is ample room for the fibers to crimp freely and shrink. If the filaments are not free from all tension, as for example, when they are allowed to relax only partially in a wash and bleach machine by hanging skeins on a rod under the weight of a large amount of liquid, the results are found to be unsatisfactory. This time of immersion of the filaments in the relaxing bath is not critical. Under the proper conditions of relaxation, the crimp will be formed in the fibers in the relaxing bath practically instantaneously. It was considered unexpected and surprising that yarns spun under the above described conditions would develop crimp on relaxing in a swelling medium after the yarn had been subjected to washing treatments and other purification treatments, and even after the yarn had been dried prior to relaxation.

This first embodiment of the invention is specifically illustrated in Examples I–XII inclusive.

In accordance with the second subgeneric embodiment of the invention, which applied more particularly to viscose containing from 3.5% to 5% alkali, the following conditions will produce an excellent grade of crimped fibers having unique characteristics described in detail later on:

1. The viscose solution must have a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 1.5 and 6.
2. The coagulating and regenerating bath must have a sulfuric acid content of between 3.5% and 6.5%.
3. The coagulating and regenerating bath must have a sodium sulfate content of between 18% and 30%.
4. The coagulating and regenerating bath must have a zinc sulfate content of between 0.1% and 2.5%.
5. The filaments must have a travel of at least 50 inches in the coagulating and regenerating bath.
6. There must be a total spinning tension on the filaments in the coagulating and regenerating bath and in the secondary stretching bath of at least 0.5 gram per denier and a total stretch of at least 40%.
7. The temperature of the coagulating bath must be between 40° C. and 75° C.
8. The temperature of the secondary stretching bath must be between 50° C. and 100° C.

9. The temperature of the relaxing bath must between 0° C. and 120° C.
10. The relaxing bath is preferably a liquid having a stronger swelling action on the filaments than water, for example 1%–5% sodium hydroxide solution.

The use of a secondary stretching bath is essential in this second embodiment of the invention. What has been said of the stretching bath in connection with the first embodiment, where its use is optional, applies equally well here. The conditions of relaxation are also the same, except that in this case it is specially desirable that the stretching bath have a positive swelling action on the filaments. The relaxing bath is preferably a dilute (1%–5%) solution of caustic alkali.

As in the case of viscose containing more than 5% alkali, the following table will be useful to show both the operable and "median" ranges in this second embodiment:

	Operable Range	Median Range
Alkali content of viscose	3.5–5%	3.75–4.24%.
Salt index of viscose	1.5–6	3.5–5.5.
Acid content of spinning bath	3.5–6.5%	3.75–4.5%.
Sodium sulfate in spinning bath.	18–30%	19–25%.
Zinc sulfate in spinning bath	0.1–2.5%	0.85–1.5%.
Total travel in both baths	Over 50 inches	Over 75 inches.
Total spinning tension	Over 0.5 g. p. d.	Over 0.5 g. p. d.
Temperature of primary bath	40–75° C.	50–60° C.
Temperature of stretching bath.	50–100° C.	60–100° C.
Temperature of relaxing bath	0–120° C.	60–100° C.

With regard to the temperature of the relaxing bath, it is generally desirable to employ lower relaxing bath temperatures with dilute caustic relaxing baths than when water is used. For example, a relaxing bath containing 3.5% caustic soda operates particularly well at 35° C.

As in the first subgeneric embodiment, the most important bath variable is the acidity, and this can readily be adjusted by means of the general formula discussed above.

This embodiment of the invention is specifically illustrated in Examples XIII and XIV.

In accordance with the third subgeneric process of the present invention, which is particularly useful where a low alkali (between 3.5% and 5%) viscose is employed and where the use of a single bath is preferred, the following relationship factors, if observed, will produce a particularly desirable crimped yarn:

1. The viscose solution must have a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 1.5 and 6.
2. The viscose solution must contain between 0.01% and 1% of a viscose-dispersible salt of a metal whose hydroxide is amphoteric.
3. The coagulating and regenerating bath must have a sulfuric acid content of between 4% and 6%.
4. The coagulating and regenerating bath must have a sodium sulfate content of between 18% and 30%.
5. The coagulating and regenerating bath must have a zinc sulfate content of between 0.1% and 2.5%.
6. The filaments must have a travel of at least 50 inches in the coagulating and regenerating bath.
7. The spinning tension on the filaments in the coagulating and regenerating bath must be at least 0.5 gram per denier and the filaments

during spinning must be stretched at least 40%.

8. The temperature of the coagulating bath must be between 40° C. and 75° C.
9. The temperature of the relaxing bath must be between 20° C. and 120° C.

Water-soluble salts of the following metals, whose hydroxides are amphoteric, are viscose-dispersible and have been added to viscose in accordance with the present invention and are known to be operative: zinc, antimony, beryllium, aluminum, cadmium, chromium, lead, iron, copper, cobalt, bismuth, and tin. Water-soluble salts of nickel are also found to be operative for this purpose. Although the amphoteric properties of nickel hydroxide are not clearly established, the latter is considered to be amphoteric in view of its close relationship to iron and cobalt and, therefore, for the purposes of the present invention, it shall be considered as being included in the above-mentioned generic grouping.

The viscose-dispersible salts may be added at any convenient stage before spinning. They are preferably added prior to the final stages of ripening of the viscose. The salt is preferably added in quantities between 0.01% and 1%, based on the weight of the viscose. The word "viscose" when used herein has its usual meaning of the total solution of cellulose xanthate in aqueous alkali.

The following table will be useful to show both the operable and median ranges when a viscose containing 3.5% to 5% alkali and modified with a salt of an amphoteric metal is used:

	Operable Range	Median Range
Alkali content of viscose	3.5–5%	3.75–4.25%.
Salt index of viscose	1.5–6	3.5–5.5.
Metal salt content of viscose	0.01–1%	0.1–0.5%.
Acid content of spinning bath	4.0–6.0%	4.0–5.0%.
Sodium sulfate in spinning bath.	18–30%	19–25%.
Zinc sulfate in spinning bath	0.1–2.5%	0.85–1.5%.
Length of bath travel	Over 50 inches	Over 75 inches.
Spinning tension	Over 0.5 g. p. d.	Over 0.5 g. p. d.
Temperature of spinning bath	40–75° C.	50–60° C.
Temperature of relaxing bath	20–120° C.	60–100° C.

Here again, the bath acidity may be adjusted according to the general formula previously laid down.

Some of the metals disclosed above and in the Examples are less satisfactory than others, either because they do not produce as high or durable a crimp, or because they impart color to the finished filament. Nevertheless, they are all operable in the process of this invention and they all come within its scope. The salts suitable for this process include salts of inorganic acid (e. g., sulfuric or nitric acids) and organic acids (e. g., acetic or propionic acids). Sulfates are in general preferred since they introduce no extraneous ions in the coagulating bath.

This embodiment of the invention is specifically illustrated in Examples XV and XVI.

Crimped yarns or fibers made in accordance with the present invention may be produced in filament deniers ranging from 1 to 15, or even higher. A decrease in filament denier, other conditions being equal, seems to favor a slight increase in the degree of crimp obtained.

The following examples which are not to be considered limitative of the present invention illustrate in detail specific steps by which the present invention may be carried out.

Example I

A commercial type of viscose made from cotton linters and containing 7% cellulose and 6% alkali is spun at a sodium chloride index of 4.0, using a precious metal spinneret and an aqueous regenerating bath comprising 8.00% sulfuric acid, 19% sodium sulfate and 1.5% zinc sulfate at a temperature of 55° C. The thread formed in this manner is made to pass around roller guides in the spinning bath to develop tension and the bath travel used is approximately 130 inches at a spinning speed of approximately 2500 inches per minute. The tension on the thread at the point of its emergence from the bath is approximately 1 gram per denier, and the filaments are of approximately 3.75 denier each. The thread is wound on a bobbin and then cut into length of about 2½ inches after which it is dropped into a bath of water heated to 80° C. to 90° C. In the hot water, the staple fiber spontaneously crimps and retains this crimped form substantially unchanged through the steps of washing and drying which follow. If, after repeatedly tensioning the staple fibers to gradually work the crimp out of the same, they are placed in a swelling liquid in a completely relaxed state, the crimp is instantaneously restored.

Example II

Viscose thread is spun exactly as in Example I except that the thread is not cut into staple but washed on the bobbin, twisted (4 turns per inch) while maintained in a wet condition and afterwards relaxed in a bath of hot water in the form of loose skeins. Other modifications based on the production of continuous filament, crimped yarn by this invention include relaxing of the yarn in an untwisted condition, and drying of the yarn on the bobbin before subjecting it to the relaxing treatment.

Example III

Viscose similar to that used in Example I is spun into a bath containing 8.5% sulfuric acid, 19% sodium sulfate, 0.85% zinc sulfate and 4% glucose. The temperature of the bath is 45° C. with a tension on the thread of 0.5 gram per denier. Bath travel, spinning speeds and other conditions are similar to those given in Example I. The fiber produced in this way is almost equally as well crimped as that obtained from Example I.

Example IV

Viscose similar to that used in Example I is spun as before under tension of about 1 gram per denier into a regenerating bath containing 8.25% sulfuric acid, 19% sodium sulfate and 0.85% zinc sulfate. The crimped fiber produced by relaxing the cut staple in water is exactly the same as that obtained in Example I.

Example V

Viscose similar to that used in Example I is spun into fibers of 1.5 denier each at a tension of 0.5 gram per denier per filament using a regenerating bath comprising 8.5% sulfuric acid, 23% sodium sulfate, and 0.85% zinc sulfate at a temperature of 55° C. The resulting crimped fibers are exceedingly soft and have a pleasing, loose, full hand similar to that of wool.

Example VI

Viscose made from a good grade of wood pulp and having approximately the same composition as regards cellulose and alkali content as that

used in Example I is spun in a manner similar to that of Example I. The relaxed fibers are equally well crimped as those of Example I.

Example VII

Cotton linters viscose similar to that of Example I is ripened to a salt index of 1.9 and spun into a coagulating bath under conditions of long bath travel (130 inches) and high tension (0.9 gram per denier). The regenerating bath used in this case contains 7.5% sulfuric acid, 19% sodium sulfate and 1.5% zinc sulfate. The resulting fibers, although not as well crimped as those produced in Example I, probably because of the low salt index viscose used, are nevertheless quite curly and crimped and wool-like in general appearance and hand.

Example VIII

Viscose similar to that of Example I is spun at a salt index of 5.4 using a regenerating bath containing 8.5% sulfuric acid, 19% sodium sulfate and 1.5% zinc sulfate. The tension, bath travel and method of relaxing the yarn are similar to those of Example I. The product is also similar to that of Example I.

Example IX

Viscose similar to that of Example I except that it is not permitted to ripen to the same extent and therefore has an index of 5.4 instead of 4.0 is spun under a tension of 1 gram per denier into a coagulating and regenerating bath containing 9.5% sulfuric acid, 19% sodium sulfate and 2.5% zinc sulfate at a temperature of 55° C. The bath travel, spinning speed and other conditions used are the same as in Example I. The product, after relaxing in hot water, is crimped and wool-like in appearance.

Example X

Viscose similar to that of Example I is spun into a bath containing 6.75% sulfuric acid, 15% sodium sulfate, 1.5% zinc sulfate at a temperature of 45° C. The spinning tension is 0.75 gram per denier, but the other conditions, including bath travel and spinning speed are the same as in Example I. On relaxing the product in hot water, highly crimped fibers similar to those from Example I are obtained.

Example XI

Viscose similar to that of Example I is spun under a tension of 1 gram per denier into a bath containing 9% sulfuric acid, 30% sodium sulfate and 0.85% zinc sulfate. Other details of the spinning procedure and method of relaxing the yarn in water are the same as those in Example I. The product is also similar to that of Example I.

Example XII

Viscose similar to that of Example I is spun into a bath containing 8% sulfuric acid, 23% sodium sulfate, 0.85% zinc sulfate and 4% glucose. Other details of the spinning procedure and method of relaxing the yarn are similar to those of Example I. The product is obtained in the form of highly crimped fibers also similar to those of Example I.

Example XIII

A commercial type of viscose containing 7% cellulose and 4% alkali, and having a salt index of 4.2 (Reinthaler-Rowe) is spun through a precious metal spinneret in an aqueous coagu-

lating and regenerating bath comprising 4% sulfuric acid, 25% sodium sulfate and 1% zinc sulfate and having a temperature of 52° C. The yarn formed in this manner is made to pass about a convergence guide located 17½ inches from the spinneret and around roller guides in the spinning bath to develop tension. The yarn travels in this bath a total of 240 inches from the convergence guide to the draw-off roller. The tension on the yarn at the draw-off roller is 0.23 gram per denier, which results in a stretch in the yarn from the convergence guide to the draw-off roller of 36.8%. The yarn is then led into a second bath composed of water at 60° C. from which it is withdrawn by another draw-off roller. A tension of 0.67 gram per denier is applied to the yarn at this draw-off roller, resulting in a stretch in the water bath of 24.2%. The total stretch, therefore, which is applied to the yarn, is 69.8%. The yarn so produced is composed of 1200 filaments of 5.5 denier each. The yarn is wound on a bobbin and then cut into lengths of about 2½ inches, after which it is dropped into an aqueous solution containing 3.5% caustic soda at a temperature of 35° C. In this relaxing bath, the staple fibers are spontaneously crimped and retain this crimped form substantially unchanged through the steps of washing and drying which follow. If, after repeatedly tensioning the staple fibers to work the crimp gradually out of the same, they are placed in a liquid in a completely relaxed state, the cramp is instantaneously restored.

Example XIV

A commercial type of viscose containing 7% cellulose and 4% alkali, and having a salt index of 4.8 (Reinthaler-Rowe) is spun through a precious metal spinneret in an aqueous coagulating and regenerating bath comprising 3.98% sulfuric acid, 25.1% sodium sulfate and 1.48% zinc sulfate and having a temperature of 52° C. The yarn formed in this manner is made to pass about a convergence guide and around roller guides in the spinning bath to develop tension. The yarn travels in this bath a total of 215 inches from the convergence guide to the draw-off roller. The tension on the yarn at the draw-off roller is 0.25 gram per denier, which results in a stretch in the yarn from the convergence guide to the draw-off roller of 21.8%. The yarn is then led into a second bath composed of water at 60° C. from which it is withdrawn by another draw-off roller. A tension of 0.5 gram per denier is applied to the yarn at this draw-off roller, resulting in a stretch in the water bath of 35%. The total stretch, therefore, which is applied to the yarn is 64.5%. The yarn produced is composed of 1800 filaments of 3.0 denier each. The yarn is wound on a bobbin and then cut into lengths of about 2½ inches, after which it is dropped into an aqueous solution containing 3.5% caustic at a temperature of 35° C. In this relaxing bath, the staple fibers are spontaneously crimped and retain this crimped form substantially unchanged through the steps of washing and drying which follow. If, after repeatedly tensioning the staple fibers to work the crimp gradually out of the same, they are placed in a liquid in a completely relaxed state, the crimp is spontaneously restored.

Example XV

A viscose containing 7% cellulose and 4% alkali is prepared in a conventional manner from wood pulp, except that during the mixing of the cellulose xanthate with water, prior to ripening, 0.1% of zinc sulfate (based on the weight of the viscose) is added to the solution. The resulting dispersion is ripened to a salt index of 4.4 and then forced through a precious metal spinneret into a regenerating bath comprising 4.6% sulfuric acid, 25% sodium sulfate, and 0.85% zinc sulfate. The precious metal spinneret contains 40 openings of such a size as to form 150 denier thread. The total bath travel in the coagulating and regenerating bath is approximately 130 inches, and the spinning tension on the thread is approximately 0.9 gram per denier. This long bath travel and high tension are obtained by the use of a suitable system of guides and rollers in the bath which are adapted to impart a gradually increasing tension on the thread. The temperature of the coagulating bath is 55° C. The thread is collected on a bobbin and, immediately after collection, is cut from the bobbin into lengths of about 2 inches and permitted to fall into a bath of water heated to about 90° C. Upon striking the water, the threads spontaneously crimp to a very marked extent and resemble wool in appearance. The crimp is durable and resistant to washing.

Example XVI

To viscose similar in cellulose and alkali content to that used in Example XV is added 0.1% copper sulfate based on the weight of the total viscose solution. This viscose is ripened to an index 4.0 and spun under a tension of 1.1 grams per denier into a coagulating and regenerating bath containing 4.6% sulfuric acid, 25% sodium sulfate and 0 85% zinc sulfate. The bath travel, temperature of the bath, etc. are the same as in Example XV. The yarn produced is of a greenish-brown color. Upon relaxing this yarn in hot or cold water, highly crimped fibers are obtained.

Further in accordance with this particular embodiment of the invention, excellently crimped yarns can be obtained by spinning viscose under the conditions summarized in the table below, the bath travel being in all cases approximately 130 inches and the bath temperature 55° C.:

Cellulose content of viscose	Alkali content of viscose	Metal Salt in viscose	Salt Index of viscose	H_2SO_4 in bath	Na_2SO_4 in bath	$ZnSO_4$ in bath	Tension
				Per cent	*Per cent*	*Per cent*	*G. p. d.*
7	4	0.5% $ZnSO_4$	4.4	4.1	25	0.85	1.0
7	4	0.1% $NiSO_4$	4.0	4.75	25	0.85	1.1
7	4	0.1% Pb $(OCOCH^3)_2$	4.0	4.59	25	0.85	1.0
7	4	0.1% $Al^2(SO^4)_3$	4.0	4.6	25	0.85	1.1
7	3.5	0.1% $CdSO_4$	5.5	4.0	30	0.85	0.8
7	5	0.1% Al $(OCOCH_3)_3$	4.0	6.0	18	0.85	0.9

The value of the general formula

$$A=\left[\frac{(KC.N)}{100}\right]x$$

will be apparent by consideration of the following table, which indicates the minimum gel swelling acidity and the acidity range within which maximum crimp is obtained for the various viscose compositions used in several of the examples.

Example	Viscose Characteristics				Spinning Bath Characteristics					System Characteristics	
	Cellulose Conc.	Caustic Conc.	Index		Temp.	H_2SO_4 Conc.	Na_2SO_4 Conc.	$ZnSO_4$ Conc.	Glucose Conc.	(X) MGS Acidity	(A) Spinning acidity range as calculated
	Per Cent	*Per Cent*			*°C.*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*	*Per Cent*
I	7	6	4.0		55	8.0	19	1.5		9.0	7.1-9.2
II	7	6	4.0		55	8.0	19	1.5		9.0	7.1-9.2
III	7	6	4.0		45	8.5	19	0.85	4.0	9.3	7.5-9.7
IV	7	6	4.0		55	8.25	19	0.85		9.4	7.5-9.8
V	7	6	4.0		55	8.5	23	0.85		9.2	7.4-9.6
VI	7	6	4.0		55	8.0	19	1.5		9.0	7.1-9.2
VII	7	6	1.9		55	7.5	19	1.5		8.3	6.7-8.7
VIII	7	6	5.4		55	8.5	19	1.5		8.75	7.0-9.1
IX	7	6	5.4		55	9.5	19	2.5		9.75	7.8-10.2
X	7	6	4.0		45	6.75	15	1.5		7.8	6.8-8.2
XI	7	6	4.0		55	9.0	30	0.85		10.8	8.6-11.3
XII	7	6	4.0		55	8.0	23	0.85	4.0	9.2	7.4-9.6
XIII	7	4	4.2		52	4.0	25	1.0		6.8	3.6-4.7
XIV	7	4	4.8		52	3.98	25.1	1.48		6.6	3.5-4.6
XV	7	4	4.4	0.1% $ZnSO_4$	55	4.6	25	0.85		6.6	3.5-4.62
XVI	7	4	4.0	0.1% $CuSO_4$	55	4.6	25	0.85		6.2	3.5-4.6

$$\text{Max. } A = \frac{2.5\,(C)\,(N)}{100}X$$

$$\text{Min. } A = \frac{1.9\,(C)\,(N)}{100}X$$

The variation in the range is explained by the fact that some systems have very flat minimum gel swelling curves near the minimum gel swelling point.

The crimped fibers produced by this process are entirely new and different in character from previously known crimped fibers. They are characterized by unique and outstanding properties not found in the crimped fibers produced heretofore. One of these entirely new and unexpected properties lies in the fact that the crimp, after being removed through stretching, combing, or other mechanical treatment, is substantially completely restored to the fiber simply by suspending it in water, or other aqueous liquid, in the absence of tension. The crimp regain is practically instantaneous, whether the fiber treated be in the form of staple or of continuous filaments. It can be readily demonstrated by manually stretching, or repeatedly combing a sample of crimped fiber so as to destroy its crimp, then immersing the sample in water, whereupon it at once crinkles and crimps to give the original structure. This surprising property is, of course, of great importance in the industrial processes to which the fibers may be subjected. For example, carding usually destroys, at least partly, the crimp in an ordinary crimped fiber. Fibers made by this process, however, may be carded and afterward immersed in water, whereby the original crimp is restored completely or substantially so. No previously known crimped regenerated cellulose fibers even remotely possess this remarkable characteristic.

It is theorized that the production of crimped high tenacity fibers according to this invention is possible primarily by reason of the fact that during spinning there is formed in individual filaments a certain kind of non-uniformity with respect to the orientation of the cellulose comprising the edges or outside boundary of the filament as compared with that comprising the interior sections of the filament. When fibers possessing such non-uniformity in their cross sections are permitted to shrink freely, the different layers of regenerated cellulose do not shrink to the same extent and the fibers tend spontaneously to fold over and produce a crimped effect. For this reason, use is made of the high spinning tensions which are a fundamental feature of the present invention. A proper balance between the above described relationship factors is considered to be essential since only under such selected conditions is the rate of penetration of acid into the thread such that a good differentiation can be obtained between the degree of orientation of fiber wall and fiber core. There is a possibility that differences in the fiber structure (density and degree of orientation) occur across the filament which ultimately cause the fiber to crimp when relaxed. The foregoing theoretical discussion is not, however, to be construed as limiting the process of this invention.

The high tenacity crimped fibers which may be obtained as a result of the present invention are characterized by filament strength of from 2.25 to over 3 grams per denier dry tenacity, and from 1.25 to over 2 grams per denier wet tenacity. The dry extensibilities, after straightening the crimp therefrom, for threads formed in accordance with the present invention are of the order of 10% to 20%, depending on the spinning tension used in their formation, and in general, it can be said that the extensibilities of crimped fibers produced in accordance with the present invention are better than those of straight fibers of equal tensile strength but spun without permitting free shrinkage. The curly crimp in the fibers produced in accordance with the present invention is durable and produces a pleasing, wool-like appearance and hand. In the case of fibers which have been cut to staple length before being permitted to relax in water, the crimps obtained are quite irregular, both as to their number per inch and their arrangement around the fiber axis. It is difficult, therefore, to define the degree of crimp obtained in these fibers in a quantitative manner, but in general, it may be said that the number of crimps per unit length along the axis of the unstretched fiber is above 10 crimps per inch. This means that these fibers are easily distinguishable from ordinary regenerated cellulose staple fibers, even those made by the so-called "acid-cutting" process, since at most the latter do not show more than 5 or 6 crimps per inch. The crimps in the fibers are

535

remarkably resistant to laundering with soap. As has been mentioned previously, even after removing the crimp by stretching the filaments, the crimp can be restored by subjecting the filaments or fibers to another relaxing treatment in a liquid.

Continuous filament yarn comprising crimped filaments of the type hereinabove described is particularly desirable for the production of woven and knit goods where more than average yarn strength, together with a wool-like hand, is desired. The crimped staple fibers of the present invention are very desirable for the production of a unique and superior spun yarn. Fabrics produced from both continuous filament and spun yarn made in accordance with the present invention will have a very desirable hand, due to regain of filament and fiber crimp upon wetting.

Since it is obvious that many changes and modifications can be made in the above described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the said details except as set forth in the appended claims.

I claim:

1. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%; and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

imposing on said filaments, during the spinning thereof, a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in a liquid which will swell the same at a temperature of between 0° and 120° C.

2. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5;
C is the cellulose content in per cent by weight of the viscose and is approximately 7%;
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%; and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline stretching bath containing not to exceed that acidity equivalent to 3% sulfuric acid, imposing on said filaments, during the spinning thereof, a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in a liquid which will swell the same at a temperature of between 0° and 120° C.

3. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline stretching bath containing not to exceed that acidity equivalent to 3%

sulfuric acid and having a temperature between 50° C. and the boiling point thereof, imposing on said filaments during the spinning thereof, a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in a liquid which will swell the same at a temperature of between 0° and 120° C.

4. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline, aqueous stretching bath having a temperature between 50° C. and the boiling point thereof, imposing on said filaments during the spinning thereof a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in a liquid which will swell the same at a temperature of between 0° and 120° C.

5. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,

N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline stretching bath containing not to exceed that acidity equivalent to 3% sulfuric acid, imposing on said filaments during the spinning thereof a tension of at least 0.5 gram per denier and a stretch of at least 40%, at least a portion of said stretch being imposed on the filaments in the spinning bath and a portion of said stretch being imposed on the filaments in the stretching bath, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in a liquid which will swell the same at a temperature of between 0° and 120° C.

6. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline stretching bath containing not to exceed that acidity equivalent to 3% sulfuric acid, imposing on said filaments during the spinning therof a tension of at least 0.5 gram per denier and a stretch of at least 40%, the greater portion of said stretch being imposed on the filaments in the stretching bath and the smaller portion of said stretch being imposed on the filaments in the spinning bath, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from

all tension, in a liquid which will swell the same at a temperature of between 0° and 120° C.

7. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

imposing on said filaments, during the spinning thereof, a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in water at a temperature of between 0° and 120° C.

8. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline stretching bath containing not to exceed that acidity equivalent to 3% sulfuric acid, imposing on said filaments, during the spinning thereof, a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in water at a temperature of between 0° and 125° C.

9. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,
K is a factor which may have any value from 1.9 to 2.5,
C is the cellulose content in per cent by weight of the viscose and is approximately 7%,
N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and
x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline stretching bath containing not to exceed that acidity equivalent to 3% sulfuric acid and having a temperature between 50° C. and the boiling point thereof, imposing on said filaments during the spinning thereof a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in water at a temperature of between 0° and 120° C.

10. A process for the production of highly crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments from a balanced viscose-sulfuric acid-salt spinning bath system in which the spinning bath contains 0.1% to 3.0% zinc sulfate and a substantial amount of sodium sulfate and in which the sulfuric acid content of the spinning bath is of the order of 11.3% or less and is in accord with the formula:

$$A=\left[\frac{K(C.N)}{100}\right].x$$

wherein

A is the sulfuric acid content in per cent by weight of the spinning bath and is less than x,

K is a factor which may have any value from 1.9 to 2.5,

C is the cellulose content in per cent by weight of the viscose and is approximately 7%,

N is the sodium hydroxide content in per cent by weight of the viscose and is at least 3.5%, and

x is the percentage content by weight of sulfuric acid in the spinning bath which will produce a regenerated cellulose filament having the minimum gel swelling factor with the viscose specified by C and N, said viscose having a salt index of between 1.5 and 6.0 and said bath having a sodium sulfate content of between 15% and 30% with a filament travel of at least 50 inches in the coagulating and regenerating bath and said bath having a temperature of between 50° and 75° C.

passing said filaments in the spinning thereof through a non-alkaline, aqueous stretching bath having a temperature between 50° C. and the boiling point thereof, imposing on said filaments during the spinning thereof a tension of at least 0.5 gram per denier and a stretch of at least 40%, and, after substantially complete regeneration of said filaments, relaxing the same, completely free from all tension, in water at a temperature of between 0° and 120° C.

11. A process as defined in claim 1 in which the filaments are relaxed in the relaxing bath immediately after stretching the same.

12. A process as defined in claim 1 in which the filaments are collected on a yarn support and subjected to a washing treatment after stretching and prior to relaxation.

13. A process as defined in claim 1 in which the filaments are collected on a yarn support and subjected to a washing and drying treatment after stretching and prior to relaxation.

14. A process for the production of crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments, under tension, from a viscose solution into a coagulating and regenerating bath, and after substantially complete regeneration of said filaments, freely suspending the filaments, in filamentous structure form, in an aqueous liquid bath in complete absence of tension to completely relax the same, said steps being carried out in accordance with the following critical relationship factors:

(*a*) The viscose solution must have an alkali content (calculated at NaOH) of 5% to 6.25%.

(*b*) The viscose solution must have a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 1.5 and 6.

(*c*) The coagulating and regenerating bath must have a sulfuric acid content of between 6.5% and 9.5%.

(*d*) The coagulating and regenerating bath must have a sodium sulfate content of between 15% and 30%.

(*e*) The coagulating and regenerating bath must have a zinc sulfate content of between 0.1% and 3%.

(*f*) The filaments must have a travel of at least 50 inches in the coagulating and regenerating bath.

(*g*) The spinning tension on the filaments in the coagulating and regenerating bath must be at least 0.5 gram per denier and the filaments during the spinning thereof must be stretched at least 40%.

(*h*) The temperature of the coagulating bath must be between 40° C. and 75° C.

(*i*) The temperature of the relaxing bath must be between 20° C. and 120° C.

and not more than one of said critical factors lie outside of the following range for the indicated factors:

(*j*) Salt index of viscose	3.5 to 5.5
(*k*) Sulfuric acid content of the bath	7.5% to 8.5%
(*l*) Sodium sulfate content of the bath	19% to 25%
(*m*) Zinc sulfate content of the bath	0.85% to 2.0%
(*n*) Length of bath travel	Over 75 inches
(*o*) Temperature of coagulating bath	50° C. to 60° C.
(*p*) Temperature of relaxing bath	60° C. to 100° C.

15. A process as defined in claim 14 in which the relaxing treatment liquid is water.

16. A process as defined in claim 14 in which the relaxing treatment liquid comprises an aqueous solution of an alkaline material taken from the group consisting of sodium hydroxide and sodium carbonate.

17. A process for the production of crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments, under tension, from a viscose solution into a coagulating and regenerating bath, and after substantially complete regeneration of said filaments, freely suspending the filaments, in filamentous structure form, in an aqueous liquid bath in complete absence of tension to completely relax the same, said steps being carried out in accordance with the following critical relationship factors:

(*a*) The viscose solution must have an alkali content (calculated as NaOH) of between 5.75% and 6.25%.

(*b*) The viscose solution must have a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 3.5 and 5.5.

(*c*) The coagulating and regenerating bath must have a sulfuric acid content of between 7.5% and 8.5%.

(*d*) The coagulating and regenerating bath must have a sodium sulfate content of between 19% and 25%.

(*e*) The coagulating and regenerating bath must have a zinc sulfate content of between 0.85% and 2%.

(*f*) The filaments must have a travel of at least 75 inches in the coagulating and regenerating bath.

(*g*) The spinning tension on the filaments in the coagulating and regenerating bath must be at least 0.5 gram per denier and the filaments during the spinning thereof must be stretched at least 40%.

(*h*) The temperature of the coagulating bath must be between 50° C. and 60° C.

(*i*) The temperature of the relaxing bath must be between 60° C. and 100° C.

18. A process as defined in claim 17 in which the relaxing treatment liquid is water.

19. A process as defined in claim 17 in which the relaxing treatment liquid comprises an aqueous solution of an alkaline material taken from the group consisting of sodium hydroxide and sodium carbonate.

20. A process as defined in claim 14 which comprises subjecting the filaments to a liquid washing treatment after coagulation and prior to the relaxing treatment.

21. A process as defined in claim 14 which comprises subjecting the filaments to a liquid washing treatment, and drying, after coagulation and prior to the relaxing treatment, the temperature of the relaxing bath being at least 60° C.

22. A process as defined in claim 14 which comprises subjecting the filaments to a secondary stretching treatment in an aqueous bath having a temperature of at least 60° C. prior to the relaxing treatment.

23. A process as defined in claim 17 which comprises subjecting the filaments to a liquid washing treatment after coagulation and prior to the relaxing treatment.

24. A process as defined in claim 17 which comprises subjecting the filaments to a liquid washing treatment, and drying, after coagulation and prior to the relaxing treatment.

25. A process as defined in claim 17 which comprises subjecting the filaments to a secondary stretching treatment in an aqueous bath having a temperature of at least 60° C. prior to the relaxing treatment.

26. A process for the production of crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments, under tension, from a viscose solution into a coagulating and regenerating bath passing said filaments through a non-alkaline stretching bath, and after substantially complete regeneration of said filaments, relaxing the filaments, free from tension, in an aqueous liquid bath, said steps being carried out in accordance with the following critical relationship factors:

(a) The viscose solution must have an alkali content (calculated as NaOH) of between 3.5% and 5%.
(b) The viscose solution must have a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 1.5 and 6.
(c) The coagulating and regenerating bath must have a sulfuric acid content of between 3.5% and 6.5%.
(d) The coagulating and regenerating bath must have a sodium sulfate content of between 18% and 30%.
(e) The coagulating and regenerating bath must have a zinc sulfate content of between 0.1% and 2.5%.
(f) The filaments must have a travel of at least 50 inches in the coagulating and regenerating bath.
(g) The spinning tension on the filaments in the coagulating and regenerating bath must be at least 0.5 gram per denier and the filaments during the spinning thereof must be stretched at least 40%.
(h) The temperature of the coagulating bath must be between 40° C. and 75° C.
(i) The temperature of the secondary stretching bath must be between 50° C. and 100° C.
(j) The temperature of the relaxing bath must be between 0° C. and 120° C.

27. A process as defined in claim 26 in which the relaxing treatment liquid comprises an aqueous solution of an alkaline material taken from the group consisting of sodium hydroxide and sodium carbonate.

28. A process as defined in claim 26 which comprises subjecting the filaments to a liquid washing treatment after coagulation and prior to the relaxing treatment.

29. A process as defined in claim 26 in which the temperature of the relaxing bath is at least 60° C., and which comprises subjecting the filaments to a liquid washing treatment, and to drying, after coagulation and prior to the relaxing treatment.

30. A regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having the characteristic, when straight, of spontaneously crimping upon being suspended, free of tension, in an aqueous liquid.

31. A regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having a crimp which, upon being mechanically removed, will be substantially completely restored by suspending the filament, free from tension, in an aqueous liquid.

32. A regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having at least ten crimps per inch which, upon being mechanically removed, will be substantially completely restored by suspending the filament, free from tension, in an aqueous liquid.

33. A regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having a tenacity of at least 2.25 grams per denier and having a crimp which, upon being mechanically removed, will be substantially completely restored by suspending the filament, free from tension, in an aqueous liquid.

34. A substantially straight regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having the characteristic of spontaneously crimping, upon being suspended, free of tension, in an aqueous liquid.

35. A substantially straight regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having the characteristic of spontaneously crimping with at least ten crimps per inch, upon being suspended, free of tension, in an aqueous liquid.

36. A substantially straight regenerated cellulose filament having a non-uniformity of structure between the exterior and interior portions of the filament and having a difference of structure occurring across the filament, said filament having a tenacity of at least 2.25 grams per denier and having the characteristic of spontaneously crimping, upon being suspended, free of tension, in an aqueous liquid.

37. A process for the production of crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments under tension from a viscose solution into a coagulating and regenerating bath and, after substantially complete regeneration of said filaments, relax-

ing the filaments free from tension in an aqueous bath, said steps being carried out in accordance with the following relationship factors:

(a) The viscose solution has an alkali content (calculated as NaOH) of between 3.5% and 5%;
(b) The viscose solution has a salt index of between 1.5 and 6.0;
(c) The viscose solution contains between 0.01% and 1.0% of a viscose-dispersible salt of a metal, the hydroxide of which is amphoteric;
(d) The coagulating and regenerating bath has a sulfuric acid content of between 4% and 6%;
(e) The coagulating and regenerating bath has a sodium sulfate content of between 18% and 30%;
(f) The coagulating and regenerating bath has a zinc sulfate content of between 0.1 and 2.5%;
(g) The filaments have a travel of at least 50 inches in the coagulating and regenerating bath;
(h) The spinning tension on the filaments in the coagulating and regenerating bath is at least 0.5 gram per denier and the filaments during the spinning thereof are stretched at least 40%;
(i) The temperature of the coagulating bath is between 40° C. and 75° C.
(j) The temperature of the relaxing bath is between 20° C. and 120° C.

38. The process of claim 37 in which a stretch of at least 40% is imposed during coagulation and regeneration.

39. The process of claim 37 in which the relaxing liquid is an aqueous solution of an alkaline material.

40. A process for the production of crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments under tension from a viscose solution into a coagulating and regenerating bath and, after substantially complete regeneration of said filaments, relaxing the filaments free from tension in an aqueous bath, said steps being carried out in accordance with the following relationship factors:

(a) The viscose solution has an alkali content (calculated at NaOH) of between 3.75% and 4.25%;
(b) The viscose solution has a salt index of between 3.5 and 5.5;
(c) The viscose solution contains between 0.01% and 0.5% of a viscose-dispersible salt of a metal, the hydroxide of which is amphoteric;
(d) The coagulating and regenerating bath has a sulfuric acid content of between 4% and 5%;
(e) The coagulating and regenerating bath has a sodium sulfate content of between 19% and 25%;
(f) The coagulating and regenerating bath has a zinc sulfate content of between 0.85% and 1.5%;
(g) The filaments have a travel of at least 75 inches in the coagulating and regenerating bath;
(h) The spinning tension on the filaments in the coagulating and regenerating bath is at least 0.5 gram per denier and the filaments during the spinning thereof are stretched at least 40%;

(i) The temperature of the coagulating bath is between 50° C. and 60° C.;
(j) The temperature of the relaxing bath is between 60° C. and 100° C.

41. The process of claim 40 in which a stretch of at least 40% is imposed during coagulation and regeneration.

42. The process of claim 40 in which the relaxing treatment liquid is an aqueous solution of an alkaline material.

43. A process for the production of crimped regenerated cellulose filaments and fibers which comprises the steps of spinning filaments, under tension, from a viscose solution into a coagulating and regenerating bath, passing said filaments through a non-alkaline stretching bath, and after substantially complete regeneration of said filaments, relaxing the filaments, free from tension, in an aqueous liquid bath, said steps being carried out in accordance with the following critical relationship factors:

(a) The viscose solution has an alkali content (calculated as NaOH) of between 3.75% and 4.24%.
(b) The viscose solution has a salt index (as determined by Reinthaler-Rowe, "Artificial Silk," 1928, page 69) of between 3.5 and 5.5.
(c) The coagulating and regenerating bath has a sulfuric acid content of between 3.75% and 4.5%.
(d) The coagulating and regenerating bath has a sodium sulfate content of between 19% and 25%.
(e) The coagulating and regenerating bath has a zinc sulfate content of between 0.85% and 1.5%.
(f) The filaments have a travel of at least 75 inches in the coagulating and regenerating bath.
(g) The spinning tension on the filaments in the coagulating and regenerating bath is at least 0.5 gram per denier and the filaments during the spinning thereof are stretched at least 40%.
(h) The temperature of the coagulating bath is between 50° C. and 60° C.
(i) The temperature of the stretching bath is between 60° C. and 100° C.
(j) The temperature of the relaxing bath is between 60° C. and 100° C.

WILLIAM D. NICOLL.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,683,199	Lilienfeld	Sept. 4, 1928
2,015,201	Stockly et al.	Sept. 25, 1935
2,192,074	Givens et al.	Feb. 27, 1940
2,238,977	Jackson et al.	Apr. 22, 1941
2,249,745	Charch et al.	July 22, 1941
2,249,756	Finzel	July 22, 1941
2,267,055	Tippetts	Dec. 23, 1941
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

FOREIGN PATENTS

Number	Country	Date
481,565	Great Britain	Mar. 11, 1938
493,288	Great Britain	Oct. 3, 1938

Certificate of Correction

Patent No. 2,515,834 July 18, 1950

WILLIAM D. NICOLL

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 4, before the syllable "bal-" insert an opening quotation mark; column 6, line 73, for "both" read *bath*; column 9, line 1, after "must" insert *be*; column 13, line 33, for "cramp" read *crimp*; columns 13 and 14, in the table, under the heading "Metal Salt in viscose", line 3 thereof, for "0.1% $Pb(OCOCH^3)_2$" read *0.1% $Pb(OCOCH_3)_2$*; line 4, for "0.1% $Al^2(SO^4)_3$" read *0.1% $Al_2(SO_4)_3$*; column 14, second line below the table, for that portion of the equation reading "(KC.N)" read *K(C.N)*; column 27, line 50, for "at NaOH" read *as NaOH*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of October, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.