Dec. 20, 1949 P. H. SCHLOSSER ET AL 2,491,937

METHOD OF PRODUCING RAYON FILAMENTS FROM VISCOSE

Filed Sept. 12, 1944 2 Sheets-Sheet 1

Fig 1.

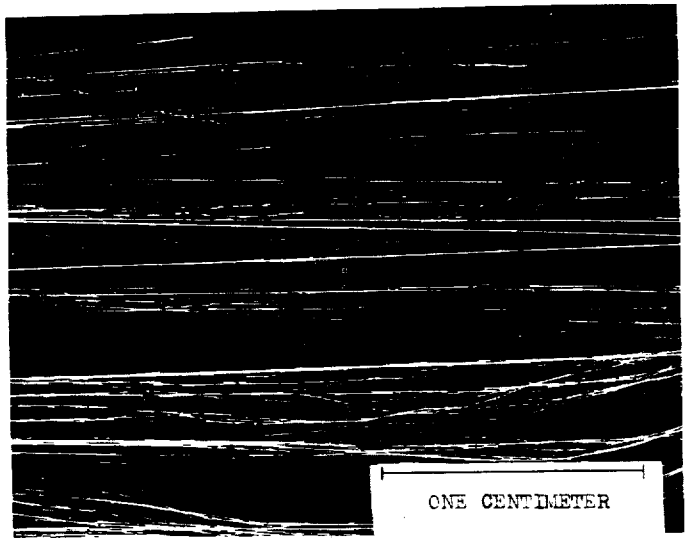
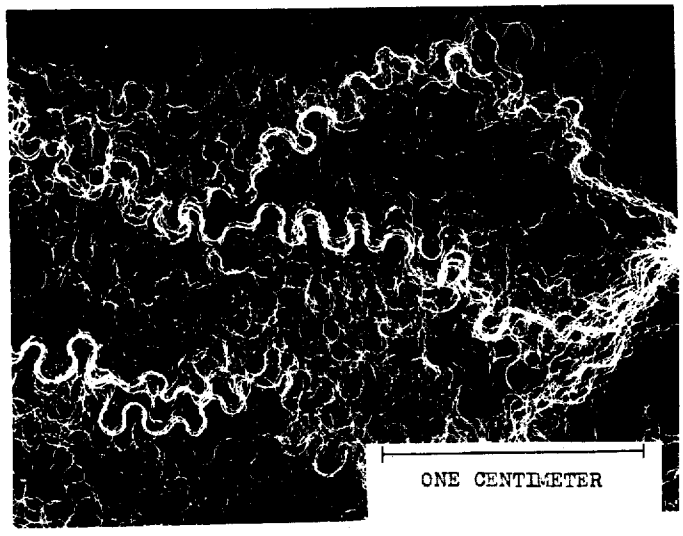


Fig 2.



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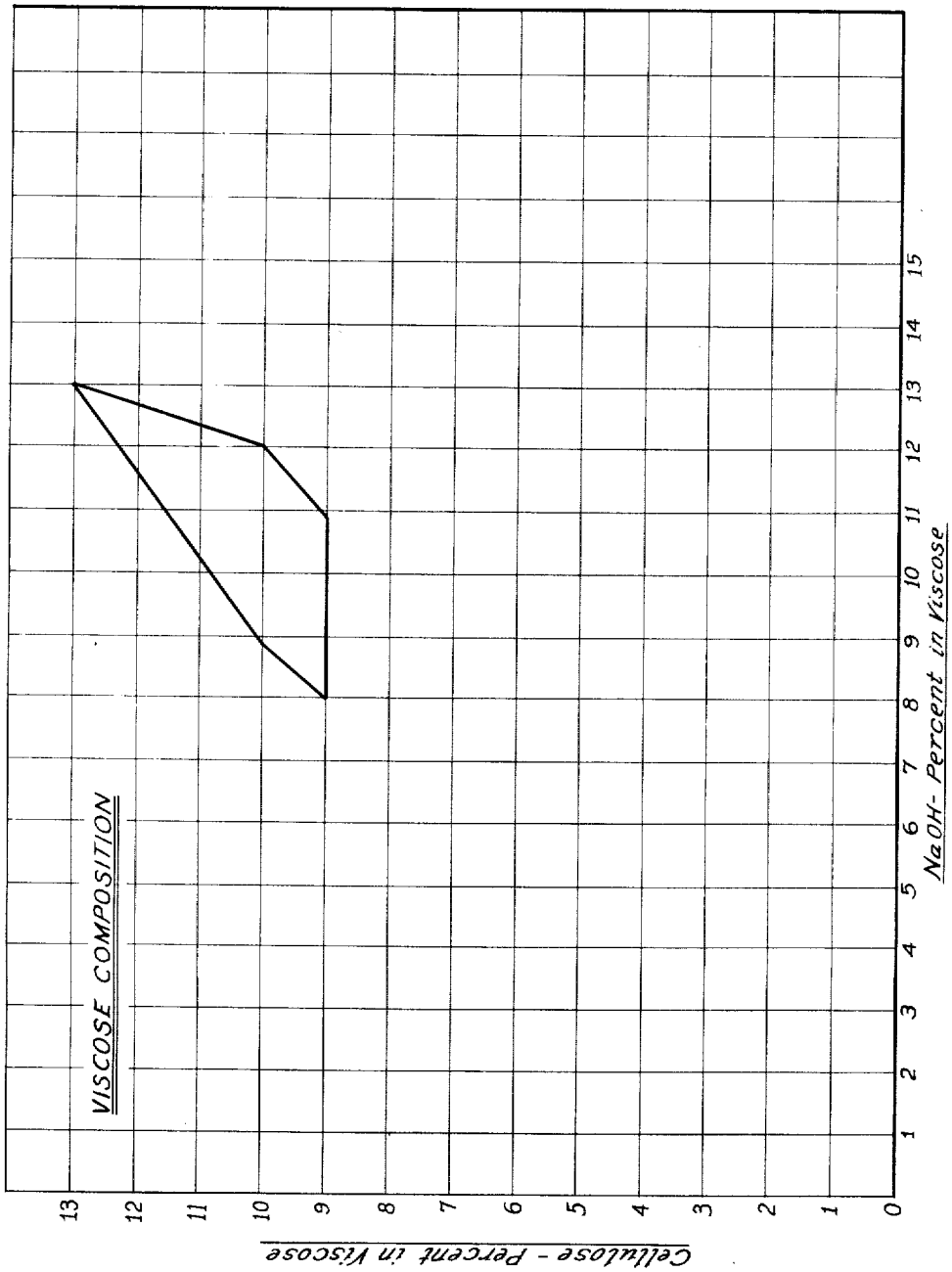


Fig. 3.

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METHOD OF PRODUCING RAYON FILAMENTS FROM VISCOSE

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15 Claims. (Cl. 18—54)

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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 aspect, is characterized by spinning a viscose solution of special composition and subjecting the extruded filaments to high tension stretching during the operation of coagulation and regeneration. The resulting regenerated and stretched cellulosic filaments have the capacity to crinkle spontaneously when treated with water under conditions permitting free shrinkage. The method of the invention not only provides a method of producing filaments having the capacity to crinkle but also a method of crinkling the filaments. The special viscose solution used in the practice of the invention is relatively high in both the cellulose and the caustic soda contents and is spun in an acid spin bath and is stretched during the operation of coagulation and regeneration. 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.

In addition to the viscose composition, which will be fully described hereinafter, another important aspect of the method of the invention is the stretching of the filaments during coagulation and regeneration and the control of the chemical state and the physical conditions in consequence of which the regenerated filaments possess the property of crinkling spontaneously when treated with water under conditions permitting free shrinkage. The stretched filaments may be prevented from shrinking by mechanical stress and subsequently washed and dried while still under stress. The dry filament produced in this manner will be straight with no apparent crinkle but will nevertheless retain its capacity to crinkle as will be evident when the filament is rewetted with water under conditions permitting free shrinkage.

Without any intention to limit the invention by any theoretical explanation of the improved results obtained thereby, the following more or less theoretical discussion is submitted largely

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for the purpose of facilitating an understanding of the invention in its various modifications:

There is evidence that the high caustic soda content of our special viscose composition of our invention retards coagulation of the inside of the filament while the outside is being coagulated and regenerated. The high cellulose content of our special viscose tends to give a rapid formation of surface skin which is more dense than with normal viscose and less easily penetrated by the acid bath. Therefore, two layers are formed of such difference in initial structure that when stress is imposed on the filament, as by stretching while still in a semi-plastic condition, the inside portion is stretched with relatively little increase in uniaxial orientation, while the outside portion becomes highly oriented along the filament axis by the stretching. As a result, unbalanced potential strains then exist between the inside and the outside portions; the oriented portion having a greater tendency to shrink than the unoriented portion. If the filament is now allowed to shrink in water (shrinking takes place along the filament axis, swelling across the axis), these strains assert themselves and are manifest in a crinkled form. This crinkled form, in which the strains are equalized, then represents the normal and stable state of the filament, whereas the straight form represents the unstable state. Again the straight, though unstable, form can exist both in the dry and wet condition of the yarn, but when wet, presence of certain salts in high concentration or the action of mechanical force is required to prevent spontaneous shrinkage and crinkling. Due to this structural origin, this type of crinkle is very permanent, and due to the residual uniaxial orientation, the tensile strength is high.

In carrying out a method of the invention, it is necessary to use a viscose solution of special composition. The special composition viscose of this invention has 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 an ordinate diagram as shown in the accompanying drawing Figure 3:

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 of 13% is approached, the ratio of caustic soda to cellulose narrows down to the preferred value of 1.0.

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 not only upon the composition of the viscose but upon the maintenance of a particular state during coagulation and regeneration, and in particular the application of a considerable degree of stretch to the yarn during spinning.

In accordance with this aspect of the invention, a viscose solution having the special composition previously described is extruded into a regenerating bath of the normal Muller type, and, while the cellulose is undergoing coagulation, the filaments are subjected to high tension stretching. The term "high tension stretching," as used herein, refers to tensions, during the operation of coagulation and regeneration, about 0.5 gm. per denier and especially to tensions of 0.75 to 1.0 gm. per denier or higher. Actually the upper limit in high tension spinning is the point where damage to the filaments is noticed—either through visible breakage, evidenced by sticking of filaments on godets or roller guides, or through noticeably poorer physical properties of the finished yarn. After regeneration and after or during washing free from spin-bath solution, the wet stretched filaments have the capacity to crinkle when free shrinkage is permitted. The filaments may be subjected to the usual after-treatments such as washing, desulfurizing, drying and the like, but when crinkling is to be avoided to make a product having the capacity to crinkle, the stretched filaments are prevented from shrinking while in a wet state. For example, the filaments may be washed and dried in package form on a bobbin without crinkling, but if wet with water while free to contract, they crinkle spontaneously.

The special viscose is extruded into or otherwise suitably contacted with a regenerating medium, e. g., in a normal Muller spin bath. A normal Muller spin 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%. As used in this application, the term "normal Muller spin bath" does not include baths containing iron in any appreciable quantity or zinc in amounts greater than 1.5%. Such special baths have a highly delayed coagulating action, and while sometimes used for stretch spinning, nevertheless, are not of the character used in this invention. 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 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 containing about 10% each of cellulose and caustic soda. The newly-formed filaments are subjected to a high degree of stretching, as soon as is feasible after extrusion into the spin bath. Numerous stretch-spinning methods are applicable, a very effective one being the progressive stretching of the filaments while in contact with the regenerating spin bath. For example, a stretching operation such as is commonly used in the production of high tenacity tire-cord yarn is very desirable. Striations in the filaments set up by stretching stresses are later manifest in irregular shrinkage forces when shrinkage is induced by treating the filaments with water, for example, by replacing the spinning bath held by the regenerated filaments with water in the process of the normal washing operation.

The stretched filaments may be taken directly from the spin bath, or they may be collected in the form of an acid cake, in a centrifugal pot or on a bobbin, and then reeled into skeins or cut into staples. At this stage, the filaments are normal in appearance and straight, but when they are washed with water and allowed to shrink freely, crinkling occurs immediately and spontaneously. It is notable that the crinkles are extremely prominent in the wet state and, of course, are retained when in the dry state. In producing dry crinkled filaments, it is necessary to dry the wet crinkled filaments while they are in a relaxed state. Moreover, in addition to possessing a high degree of crinkle, the resulting filaments have unusually high tensile strength.

The invention involves the production of a straight viscose filament having the capacity to crinkle spontaneously when treated with water in the absence of chemical conditions or physical forces which inhibit free shrinkage, such as a high concentration of certain salts that exist in the spinning solution, or a restraining force such as results from tightly winding the filaments on a bobbin.

In producing straight filaments having the capacity to crinkle, the filaments are prevented from crinkling either by washing and drying under tension or by washing under tension and impregnating the wet yarn with a solution which inhibits crinkling, e. g., a saturated solution of ammonium sulfate, methanol, etc. The result in either case is a straight product having the capacity to crinkle when treated with water under conditions permitting shrinkage.

The simplest method of producing straight filaments with a capacity to crinkle is to simply dry the washed filaments under tension. Another desirable procedure may be to lead the washed filaments while under tension through a bath

containing a saturated solution of ammonium sulfate. If the electrolyte of 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, as for instance, 1% NaOH in water or 5% dimethyl dibenzyl ammonium hydroxide in water may be particularly useful in reswelling dried fiaments for purposes of crinkling.

Treatment of the stretched 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 during spinning and 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 soduim 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 dimethyl dibenzyl 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 Muller type 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 spinnerets having holes 0.0020 of an inch in diameter. The filaments of 200 denier (total) were stretch-spun at 65 meters per minute under a tension of 200 g. applied to the strand soon after contacting the bath and while immersed in the spin bath over a path of about 40 inches. The filaments were collected in a centrifugal spinning pot, then reeled off from the acid cake into a skein and placed in a water wash. The skein direct from acid cake consisted of straight filaments, as illustrated in Fig. 1, which, however, became highly crinkled, as illustrated in Fig. 2, when placed in water and allowed to shrink freely. The crinkled filaments were then desulfured, bleached and dried. The filaments were highly crinkled, had good hand, were bulky and of dull lustre. The tenacity of the filaments was 2.5 g./denier dry, 1.5 g./denier wet; elongation (with crinkles straightened out) equalled 18% when dry and 24% when wet. The additional elongation due to crinkles was 15 to 20% for this continuous filament yarn with a twist of 3 turns per inch.

To further illustrate the invention, using the same spinning conditions given in Example I, crinkles were not obtained (1) with viscose of composition 7.5 cellulose and 6.5 sodium hydroxide spun under high tension of 1 g./denier, and (2) with viscose of composition 10% cellulose and 10% sodium hydroxide spun under low tension of 0.25 g./denier.

Example II

Viscose made from wood pulp and having the composition 9% cellulose and 9% sodium hydroxide at a sodium chloride index of 5.5 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 120 holes, each hole being 0.0030 of an inch in diameter at a rate to give filaments of 400 denier which were grouped and stretched by passing them over a series of tension wheels and then wound up on a bobbin at a speed of 80 meters per minute under a tension of 350 g. The filaments were cut into 2-inch staples and in the acid-set condition were still straight as the filaments of Fig. 1. When these straight staples were put in water, a very high crinkle developed immediately and spontaneously; the crinkled staples then having a length of only ½ inch.

Example III

Viscose with a composition of 10% cellulose and 9% sodium hydroxide, a viscosity of 100 seconds and a salt index of 6.0 was spun into a spin bath with a composition of 140 g./liter H_2SO_4, 245 g./liter Na_2SO_4, 50 g./liter glucose, 12.5 g./liter $ZnSO_4$ at 50° C. using a spinneret with 60 holes, each having a diameter of 0.0031 of an inch. The filaments of 200 denier were grouped into a thread which was stretch-spun at 60 meters per minute under a tension of 190 g. As the thread passed through the bath, it was stretched under progressively increasing tension while immersed in the spin bath. When collected in a centrifugal pot, reeled off into a skein and washed, the thread showed a fair degree of crinkle. Under the same spinning conditions, a viscose composition of 10% cellulose and 6.5% sodium hydroxide showed no tendency to crinkle, while a viscose having 10% each of cellulose and caustic soda gave excellent crinkle.

Example IV

Viscose with a composition of about 10% each of cellulose and caustic soda was spun at a salt index of 5.5 into an acid spin bath with the composition 145 g./liter H_2SO_4, 320 g./liter Na_2SO_4, 12 g./liter $ZnSO_4$ and 55 g./liter glucose at 52° C. using a spinneret with 480 holes each having a diameter of 0.0030 inch. The filaments of 1100 total denier were grouped into a thread which was drawn around a series of tension wheels submerged in the spin bath to give a bath path of about 100 inches and a tension of about 950 grams at the windup where the yarn was collected on a bobbin at a speed of 85 meters/minute. A bobbin of the yarn was washed acid free and dried on the bobbin

to yield straight yarn with capacity to crinkle. When a 4-inch staple (about 4 in. x ⅛ x 1/32) of this dry yarn was dropped into a solution of 5% dimethyl dibenzyl ammonium hydroxide in water, it crinkled immediately and spontaneously yielded a highly crinkled bulky chip only 1 inch in length and approximately ½ in. wide and ¼ in. thick. A second bobbin of the yarn was taken directly from the machine and in the acid state was cut to 4-inch staples. These staples (still straight after cutting due to inhibiting action of the Na_2SO_4) were dropped into water and crinkling took place immediately and spontaneously, resulting in a crinkled chip only ¾ inch in length. In this case, rate of crinkling was very fast and was complete almost the instant the yarn touched the water. When dried yarn above is wet in dimethyl dibenzyl ammonium hydroxide, the rate is somewhat slower due to slower penetration of water into the interior of filament and curling of filaments may be seen to take place over a period of a few seconds. If the washed yarn is cut from bobbin before drying, crinkling takes place at the instant of cutting but gives hardly as fine crinkle as when complete and instantaneous shrinkage is permitted by dropping the acid staple into a large volume of water.

Example V

Viscose with a composition of 13% each of cellulose and caustic soda was spun at a salt index of 5.0 into an acid bath with the composition 150 g./liter H_2SO_4, 330 g./liter Na_2SO_4, 15 g./liter $ZnSO_4$ and 50 g./liter glucose maintained at 50° C. using a spinneret with 120 holes. The filaments of 275 total denier were pulled through the spin bath for 20 inches at a speed of 80 m./mm., stretched 20% between positively driven rollers, passed through water at 80° C., stretched an additional 30%, cut into staples and dropped into water; crinkling occurring immediately and spontaneously. The resultant fiber was highly crinkled, had dull lustre and good hand.

By the process of the invention in its various modifications, 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 wool-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 after having once been stretched and that the crinkled form represents the normal equilibrium state. When straight yarn produced by spinning under high tension followed by washing and drying 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 spinning 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 dimethyl dibenzyl 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 which have been subjected to high tension during spinning may be preserved in the straight state if they are given a washing treatment with a substantially saturated solution of ammonium sulfate. The ammonium sulfate treated filaments are not subject to marked deterioration and since shrinkage is inhibited by the ammonium sulfate solution the filaments may be kept in the straight form, then converted 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 short 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.

The crinkled filaments of the invention possess certain characteristics which are manifest by the frequency and type of crinkles, the cross-section of the filaments, the orientation, dye absorption, X-ray diffraction, diffraction of polarized light and tensile properties.

The cellulosic products of the invention are especially suitable for use in staple fiber, in continuous filament rayon thread or yarn, and in textile fabrics made in whole or in part therefrom. The crinkled filaments of the invention, in the form of staple fiber, may be formed into thread or yarn by the textile operations commonly used in the cotton or the woolen arts without the excessive slippage between filaments which occurs when ordinary rayon staple is spun into thread. In addition to these properties, groups of the filaments, such as continuous filament yarns and spun staple fiber, are remarkably soft and bulky. In fine denier filaments, and especially in staple fiber, the product of the invention

has wool-like properties. The filaments, before or after crinkling, may be formed into threads and yarns of various kinds. The filaments may be crinkled before or after being twisted into a thread. The thread, whether crinkled or uncrinkled, may be spun, woven or knitted into various fabrics or materials. Special effects may be obtained by crinkling such fabrics or materials after they have been formed. Combinations of the filaments of the invention may include threads comprising filaments of the invention intermingled or intertwisted with fibers or threads of such materials as linen, cotton, rayon, cellulose acetate, silk, nylon, spun proteins, wool and the like. The filaments may have been crinkled before or after the combination or left straight with potential crinkle. The knitted goods and fabrics of the invention may be formed in whole or in part of such combination threads, or they may be formed with alternate arrangements giving novelty effects.

An important advantage of our invention is the providing of a simple, effective method for spinning crinkled or potentially crinkled viscose filaments in the conventional single bath commonly used for the stretch-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 in conventional stretch-spinning apparatus wherein are provided rollers, double godet wheels or other mechanical devices commonly used to give the yarn a high degree of stretch in the production of high tenacity yarn. It is to be emphasized, however, that in any case the invention provides a method for spinning crinkled filaments in a conventional single bath spinning operation of the type used for high stretch spinning, but in any case without requiring any mechanical alterations from the apparatus normally used for spinning straight filaments.

Another advantage of our invention is the provision of an extremely flexible method for changing all or a portion of a viscose rayon operation back and forth between production of crinkled and straight filaments. The spinning process of the invention uses without any changes in composition whatsoever, the same normal "Muller" spin baths commonly used in the production of straight filaments by the viscose process. With the process of the invention, the same circulating spin bath system may be used to supply different sets of spinning frames, simultaneously producing both crinkled and straight filaments.

We claim:

1. 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 viscose into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$ to form coagulated and regenerated cellulose filaments, subjecting the filaments to high tension stretching during coagulation and regeneration, washing and drying the filaments without appreciable shrinkage, whereby the dried filaments develop the potential capacity to crinkle spontaneously when treated with water.

2. 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 viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$ to form coagulated and regenerated cellulose filaments, subjecting the filaments to stretching under a tension of more than 0.5 gram per denier during coagulation and regeneration, whereby the stretched, regenerated filaments develop the capacity to form spontaneously on wetting with water a multiplicity of fine crinkles.

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 around 1 and the salt index from 4.0 to 7.5, extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$ to form coagulated and regenerated cellulose filaments, and stretching the filaments during coagulation and regeneration under high tension of more than 0.5 gram per denier but not so high as to cause appreciable breakage of the filaments.

4. 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 viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form coagulated and regenerated cellulose filaments, during coagulation and regeneration stretching the filaments under high tension, washing and drying the filaments without appreciable shrinkage, and at any time thereafter treating the dried filaments with water containing a swelling agent and permitting them to shrink freely and to crinkle.

5. 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 viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form cellulose filaments, during coagulation and regeneration subjecting the filaments to stretching under a spinning tension of at least 0.5 gram per denier, and crinkling the stretched cellulose while wet with water and under conditions permitting free shrinkage.

6. 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 viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$ and during regeneration stretching the resulting filaments under high tension, remov-

ing the regenerating medium which inhibits crinkling, and while the filaments are wet permitting them to shrink freely and to crinkle.

7. The improvement in the viscose process which comprises forming a viscose solution containing 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 viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form coagulated and regenerated cellulose filaments, during coagulation and regeneration stretching the filaments under high tension, washing and drying the stretched filaments without appreciable shrinkage, and treating the filaments with water having a compound dissolved therein which has a lyotropic action that enhances swelling and thereby crinkling the filaments.

8. The improvement in the viscose process which comprises forming a viscose solution containing 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 viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron in which sulfuric acid and sodium sulfate are present in such proportions that the bath consists substantially of $NaHSO_4$ together with some excess Na_2SO_4 to form coagulated and regenerated cellulose filaments, during coagulation and regeneration stretching the filaments under high tension, washing the freshly spun filaments with a concentrated aqueous solution to remove the acid, said solution containing a salt having a lyotropic action that reduces swelling and prevents free shrinkage of the filaments.

9. The improvement in the viscose process which comprises forming a viscose solution having about 10% each of cellulose and caustic soda, extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$ to form cellulose filaments, coagulating, regenerating and stretching the filaments under high tension, whereby said stretched filaments acquire the potential capacity to crinkle spontaneously when treated with water.

10. The improvement in the viscose process which comprises forming a viscose solution having about 10% each of cellulose and caustic soda, extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form coagulated and regenerated cellulose filaments, and during coagulation and regeneration subjecting the filaments to a tension of more than 0.5 gram per denier and without causing an objectionable breakage of filaments.

11. The improvement in the viscose process which comprises forming a viscose solution having about 10% each of cellulose and caustic soda and a salt index of 5.5 to 6.0, extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form coagulated and regenerated cellulose filaments, and during coagulation and regeneration subjecting the filaments to high tension stretching under a tension of more than 0.5 gram per denier.

12. The improvement in the viscose process which comprises forming a viscose solution having about 10% each of cellulose and caustic soda, extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form cellulose filaments, coagulating, regenerating and stretching the filaments under a tension of around 1 gram per denier, and while the stretched filaments are wet with water permitting them to shrink freely and to crinkle.

13. The improvement in the viscose process which comprises forming a viscose solution having about 10% of cellulose, and caustic soda in such amount with respect to the cellulose that the ratio of cellulose to caustic soda is from 0.833 to 1.13, extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron 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 to form coagulated and regenerated filaments, during coagulation and regeneration subjecting the resulting filaments to high tension stretching, cutting the filaments into staple fiber, and crinkling the cut filaments while shrinking.

14. The improvement in the viscose process which comprises forming a solution having about 10% each of cellulose and caustic soda, forming rayon filaments not exceeding 2 denier per filament by extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter about 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$, during coagulation and regeneration subjecting the filaments to a spinning tension of more than 0.5 gram per denier, and forming a multiplicity of fine crinkles in the filaments while the filaments are free to shrink.

15. The improvement in the viscose process which comprises forming a viscose solution having cellulose and soda contents within the range defined by a pentagon bounded by the following points located on an ordinate diagram:

9% cellulose, 8% caustic soda
9% cellulose, 10.8% caustic soda
10% cellulose, 12.0% caustic soda
13% cellulose, 13% caustic soda
10% cellulose, 8.9% caustic soda

extruding the viscose solution into a "normal Muller spin bath" free from appreciable quantities of iron and containing per liter 125 to 150 grams H_2SO_4, 235 to 330 grams Na_2SO_4 and 12 to 15 grams $ZnSO_4$ to form coagulated and regenerated cellulose filaments, during coagulation and regeneration stretching the filaments under high tension, said filaments having the capacity to crinkle spontaneously when wet with water under conditions permitting free shrinkage.

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(References on following page)

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,214,931	Leduc	Feb. 6, 1917
1,260,508	Borzykowski	Mar. 26, 1918
1,881,740	Lilienfeld	Oct. 11, 1932
2,044,885	Kleine et al.	June 23, 1936
2,364,273	Cox	Nov. 22, 1941

FOREIGN PATENTS

Number	Country	Date
353,483	Germany	May 18, 1922
386,133	Germany	Dec. 3, 1923
490,961	Germany	Feb. 14, 1930
492,279	Germany	Sept. 18, 1930
703,637	France	Feb. 10, 1931
705,917	France	Mar. 17, 1931

OTHER REFERENCES

Suvern: Die Kunstliche Seide, published by Julius Springer, Berlin, 1926, pages 488–489. Copy in Division 15.