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METHOD OF PRODUCING CELLULOSIC STRUCTURES

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This invention relates to the manufacture of regenerated cellulose structures from viscose. More particularly, the invention relates to improvements in the process of forming regenerated cellulose structures from viscose in a coagulating bath and stretching the formed structures to improve the tenacity thereof.

Although the invention is generally applicable to the preparation of filaments, yarns, films, caps, bands, ribbons and other similar structures of regenerated cellulose, it will, for convenience, be discussed with particular reference to the production of viscose rayon yarn.

It has long been known that the dry tenacity of a viscose rayon yarn can be increased by increasing the spinning tension employed in the spinning of the yarn. Such increase in tenacity is, however, generally accompanied by a decrease in elongation and loop strength of the yarn.

The presence of from 0.1% to 1.0% zinc sulfate permits the spinning of viscose rayon yarn at higher spinning tension without decreasing, to the same extent, the elongation and loop tenacity of the yarn. Generally, however, 1% represents the highest concentration of zinc sulfate which can be practicably used. Higher concentrations of zinc sulfate cause severe cratering of spinneret openings with a resultant adverse effect on the spinning operation.

It is therefore, an object of this invention to provide a process whereby regenerated cellulose structures, such as yarn, of improved physical properties can be spun without, at the same time, introducing spinning difficulties such as spinneret cratering that will make the process impractical for general use on a large scale.

It is another object of this invention to provide an improved process for the high tension spinning of regenerated cellulose structures from viscose.

It is a further object of this invention to provide a process for the production of a viscose rayon yarn possessing improved physical properties including high tenacity and desirable elongation.

Other objects of the invention will appear hereinafter.

These objects may be accomplished, in general, by the extrusion of viscose solution into a sulfuric acid spinning bath containing from 1%–8% chromic sulfate and from 0.1%–1% of zinc sulfate. The spinning bath may, of course, also contain the usual amounts of sodium sulfate, glucose, and/or ammonium sulfate.

It has now been found that the addition of 1%–8% chromic sulfate to a sulfuric acid spinning bath containing 0.1%–1% zinc sulfate will permit a higher spinning tension of the viscose rayon yarn than by the use of the zinc sulfate without the chromic sulfate in the bath. The addition of the chromic sulfate will not cause severe cratering of the spinneret openings. It is necessary, however, that the bath contain the zinc sulfate as well as the chromic sulfate in order to obtain these improved spinning properties of the bath resulting from the use of the chromic sulfate.

It has furthermore been found that the addition of the chromic sulfate to the bath will permit the lowering of the sulfuric acid content of the bath thereby lowering the rate of regeneration of the viscose and permitting the spun filaments to remain longer in a plastic state. In the plastic state, the filaments are more responsive to stretching conditions. It is thus possible to spin a viscose rayon yarn with higher spinning tension to produce stronger yarn without objectionably lowering the elongation of the yarn.

The following examples illustrate several embodiments of the invention. These examples, however, are to be considered only as illustrative of the principles of the invention and are not to be construed as limiting the scope of the invention.

Example I

Cotton linters viscose containing 7% cellulose and 6% caustic (i. e., 7–6 viscose) is allowed to ripen to a salt index of 5.0 and is spun into filaments (150 denier–60 filaments) by extruding the same through a spinneret having holes of .0035 inch diameter into a coagulating and regenerating bath comprising 7.0% H_2SO_4, 20% $NaSO_4$, 4% glucose, 0.85% $ZnSO_4$, and 5% $Cr_2(SO_4)_3$. The bundle of filaments is given a bath travel of 180 inches by using a 6-roller set-up. Sufficient vanes on the rollers and roller-end guide were used to produce a spinning tension of 1.0 g./d. The apparatus and general procedure used to lead viscose into the bath and to collect the formed thread are essentially the same as those used commercially in the so-called bobbin or spool process. The specific conditions include a temperature of 52° C. and a windup speed of 3500 inches per minute. The regenerated gel yarn is washed free of acid and salt and dried on the bobbin. The dried yarn is twisted 4 turns per inch, and tested after conditioning for 48 hours at 25° C.–50% relative humidity. The resulting

product is a high tenacity yarn which can be used for making tire cord.

The important advantage to the use of chromium sulfate is observed in the large increase in the maximum spinning tension and reduction in the degree of swelling of the gel threads particularly at this low acid content which are conducive to less operating troubles and improved yarn properties. For example, in the above bath, the gel swelling of the yarn and the maximum spinning tension which may be employed are 6.1 and 240 g. respectively, while in a similar bath containing no chromium sulfate the gel swelling of the yarn is 8.0 and the maximum spinning tension which may be employed is 188 g.

Example II

7–6 viscose is spun under a tension of 1.0 g./d. into a bath containing 8.0% sulfuric acid, 20% sodium sulfate, 4% glucose, 0.85% zinc sulfate, and 5% chromic sulfate. The apparatus and other spinning conditions were the same as those described in Example I. Immediately after collection the yarn is cut from the bobbin into staple fibers about 2–3 inches long and permitted to fall into water at 80–100° C. In the hot water, the fibers crimp spontaneously and retain the crimped form unchanged through the washing, purifying, and drying process. In the above bath the gel swelling and maximum spinning tension are 4.7 and 242 g. respectively. These are a great improvement over the values of 6.25 and 205 g. respectively obtaining in a spinning bath having the following composition; 8–25–4–0.85 (H_2SO_4-Na_2SO_4-glucose-$ZnSO_4$), which bath is optimum for production of good crimp. The above improved gel properties make it possible to spin at higher tension and produce crimped fibers with improved strength.

Example III

Filaments produced in the same manner as in Example II are allowed to dry under tension on the bobbin. When they are relaxed in hot water in the form of loose skeins continuous filament crimped yarn is obtained.

Example IV

A commercial viscose containing 7% cellulose and 6% caustic at a sodium chloride index of 5.1 is spun into an aqueous regenerating bath containing 9% sulfuric acid, 20% sodium sulfate, 4% glucose, 0.85% zinc sulfate, and 5% chromic sulfate at 52° C., the thread leaving the bath at 0.88 g./d. spinning tension. All other conditions for producing and processing of yarns are those described in Example I. The inclusion of 5% chromium sulfate in the bath specified reduces the gel swelling 20% and increases the maximum spinning tension at least 10%. The resulting conditions have made it possible to produce an improved supertenacity yarn for use in tire cord or for textile purposes.

Example V

Cotton linters viscose containing 7% cellulose and 6% caustic is spun at a sodium chloride index of 4.0 into an aqueous regenerating bath containing 11% H_2SO_4, 20% Na_2SO_4, 4% glucose, 0.85% $ZnSO_4$, and 5% $Cr_2(SO_4)_3$. For comparison another yarn is spun from a similar viscose into a bath containing $Cr_2(SO_4)_3$ but no $ZnSO_4$. In the latter case the regenerating bath employed contained 11.5% H_2SO_4, 23% Na_2SO_4, and 1% $Cr_2(SO_4)_3$. In both cases the viscose was spun into filaments (150 denier–40 filaments) by extruding the same through a spinneret having .004 inch hole size. The total travel in the coagulating and regenerating bath was approximately 140 inches; the travel was obtained by using a system of roller guides which were adapted to produce gradually increasing tension on the thread. The tension on the thread at the point of its emergence from the bath was 0.83 gram per denier. The thread was collected on a bobbin at 2500 inches per minute. Immediately after collecting, it was washed free of acid and salt and dried on the bobbin. The dried yarn was twisted 4 turns per inch, and tested after conditioning at 25° C.–50% relative humidity for 48 hours. The maximum break tension of the yarn spun in the bath containing both $ZnSO_4$ and $Cr_2(SO_4)_3$ was much higher than that of the yarn spun in the bath containing no $ZnSO_4$. The following table also shows that the use of $ZnSO_4$ with $Cr_2(SO_4)_3$ in the regenerating bath produces a yarn with a much lower gel swelling.

	Gel swelling	Max. break tension, g./d.	Spinning tension, g./d.	Tenacities, g./d.	
				Dry	Loop
11.5–23–1 (H_2SO_4-Na_2SO_4-$Cr_2(SO_4)_3$	6.5	1.0	0.83	3.0	1.44
11–20–4–0.85–5 (H_2SO_4-Na_2SO_4-glu.-$ZnSO_4$-$Cr_2(SO_4)_3$	4.24	1.4	0.83	3.12	2.07

The preferred method of operating the present invention is as follows: Chromic sulfate in an amount between 2% and 5% is dissolved in the coagulating and regenerating bath containing 7%–11% sulfuric acid, 18%–23% sodium sulfate, 0%–4% glucose and 0.5% to 1% zinc sulfate. The viscose is ripened to a salt index of between 4 and 6 and is then forced through a spinneret into the modified coagulating and regenerating bath at a temperature between 45° C. and 55° C. The filaments are stretched in the bath at a high tension (at least 0.3 gram per denier). For the production of high tenacity viscose rayon yarns for use in the preparation of tire cords with improved physical characteristics, it is particularly desirable to use the lowest sulfuric acid concentration which is practical for obtaining spinning performance. The bundle of filaments is preferably given a bath travel of from 150–250 inches by means of a multiple roller spinning set-up consisting of from 6–10 roller guides. These roller guides function to gradually apply tension to the traveling filaments, thereby orienting the micelles therein while they are still somewhat plastic.

Viscose used in the preparation of filaments in accordance with the present invention is not restricted to any type; for example, it may be prepared from cotton linters, wood pulp or mixtures of the two. The composition of the viscose may be varied; for example, it may have a cellulose content of between 3% and 12% and it may have an alkali content of between 4% and 8%. The salt index of the viscose may vary between 3 and 7. Although the above mentioned conditions are

preferred to obtain the maximum benefit from the invention, definite advantages will be obtained by carrying out the invention within the following broader limits.

The spinning bath may contain from 5% to 11% sulfuric acid, 18%–25% sodium sulfate, 0%–4% glucose, 0.1%–1% zinc sulfate and 1%–8% chromic sulfate. The presence of ammonium sulfate, magnesium sulfate and other modification agents commonly used by those skilled in the art will not interfere with the beneficial action of chromic sulfate. The temperature of the spinning bath should be maintained between 40° C. and 65° C.

The concentrations of the various substances used in the spinning bath should be adjusted to each other and to the composition of the viscose. For example, for viscose containing 7% cellulose and 6% caustic, when approximately 5% chromic sulfate is used in the spinning bath, the sodium sulfate content of the spinning bath should be maintained between approximately 18% and 23%. When glucose is omitted from the coagulating bath, the sodium sulfate content is preferably nearer the upper limit of its solubility in the bath. The optimum sulfuric acid content of the spinning bath is, of course, dependent upon the other constituents in the bath as well as such important viscose variables as cellulose and caustic content. It is necessary to increase the bath acidity as the concentration of sodium sulfate and glucose increases, while it should be decreased with the addition of chromic sulfate. As the sodium hydroxide content of the viscose is reduced from 6% to 4%, the optimum bath acidity is correspondingly lowered.

The above variables are preferably so adjusted as to produce a regenerated cellulose gel filament which has substantially the minimum gel swelling characteristics and highest break tension, properties which are usually associated with the best yarn characteristics and operating efficiency.

The gel swelling characteristic of a thread is measured in the following manner:

A single layer of thread is collected on a bobbin by manually operating the traverse mechanism with the thread spinning 3500 inches per minute with a 25 inch bath travel. The collected sample of thread is centrifuged in a spinning bucket rotating at 1400 R. P. M., for one minute, and the thread is then cut off, and weighed in a closed bottle. This sample is washed free of acid, dried in an oven at 105° C., and weighed again. The ratio between the gel weight of the yarn to the weight of the cellulose in the yarn is referred to as the "gel swelling" of the yarn. The gel strength (maximum spinning tension) of the yarn is measured with a tensiometer and actually represents the highest tension which can be applied and still have the thread strung up and spinning.

The total length of travel of the yarn in the bath should be within the range from 80–350 inches, depending on the bath composition, spinning speed, and denier of the individual filaments and the yarn. The process of the present invention is not limited to any particular spinning speed. Also, during the travel of the yarn in the spinning bath, gradual spinning tensions of from 50–80% of the breaking tension of the yarn are imposed thereon.

In the co-pending applications of William D. Nicoll, Serial No. 318,326, filed February 10, 1940, and Serial No. 318,327, filed February 10, 1940, are disclosed processes for the tension spinning of filaments for the purpose of imparting crimp thereto, when subsequently relaxed in a relaxing bath. The use of chromic sulfate together with zinc sulfate in accordance with the present invention is of great utility in processes relating to the high tension spinning of crimped filaments. Processes of this type are disclosed in Examples II and III of the present application.

The invention has been described above with particular reference to the use of single spinning baths. If desired, yarn spun in baths as discussed in detail above may be passed through a secondary water bath or a secondary dilute acid bath of varied composition and temperature wherein the yarn may be subjected to a further stretching operation such as is well known in the art. This second bath, in which a tension and stretch are imposed on the yarn, is preferably composed of water having a temperature of above 60° C. This stretching bath may, however, be acid. The acidity of this bath may be equivalent to 3% sulfuric acid, or less. The tension and stretch imposed on the filaments in the secondary stretching bath may be a continuation of the stretch and tension imparted thereto in the spinning bath.

The present invention is primarily concerned with the composition of the spinning bath employed in the high tension spinning of viscose rayon yarns. The yarns, once spun, can be purified and dried in any known manner with any of the usual purification solutions. The yarn may be spun by the bobbin or bucket process, and the yarn can be purified in the spun package form, or it can be wound into skeins and treated in that form. On the other hand, it may be purified in a continuous manner by the use of a conveyor belt or a yarn storing and advancing reel.

The present invention provides a process for the spinning of viscose rayon yarn having a high tenacity, and a high elongation.

This invention permits the production of yarn having these improvements in yarn characteristics without, at the same time, adversely affecting the continuity of the spinning operation.

The present invention furthermore, provides an improved process for the tension spinning of crimped yarn.

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

I claim:

1. In the method of producing regenerated cellulose structures by extruding viscose in an aqueous sulfuric acid spinning bath the step which comprises incorporating in said bath from 1%–8% chromic sulfate together with 0.1%–1% zinc sulfate.

2. In the method of producing regenerated cellulose structures by the spinning, under high tension (at least 0.3 gram per denier), of viscose in an aqueous sulfuric acid spinning bath the step which comprises incorporating in said bath from 1%–8% chromic sulfate together with 0.1%–1% zinc sulfate.

3. In the method of producing crimped regenerated cellulose filaments by the spinning, under high tension (at least 0.3 gram per denier), of viscose in an aqueous sulfuric acid spinning bath with a subsequent complete relaxation of said filaments in a swelling agent therefor the step which comprises incorporating in said bath from 1%–8% chromic sulfate together with 0.1%–1% zinc sulfate.

4. The method of producing regenerated cellulose structures which comprises the steps of spinning viscose in an aqueous sulfuric acid spinning bath containing from 1%–8% chromic sulfate together with 0.1%–1% zinc sulfate, passing said structures into a second bath, and stretching said structures in said second bath.

5. An aqueous sulfuric acid spinning bath for the spinning, under high tension (at least 0.3 gram per denier), of regenerated cellulose structures from viscose, said bath containing from 1%–8% chromic sulfate together with 0.1%–1% zinc sulfate.

6. An aqueous sulfuric acid spinning bath for the spinning, under high tension (at least 0.3 gram per denier), of regenerated cellulose structures from viscose, said bath containing from 5%–11% sulfuric acid, 18%–25% sodium sulfate, 0%–4% glucose, 1%–8% chromic sulfate and 0.1%–1% zinc sulfate.

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