This invention relates to the production of artificial filaments and fibers having a pronounced wool-like crimp or curl.

It has heretofore been found that filaments having outstanding crimp characteristics can be obtained by forming unsymmetrical composite filaments from two different viscous which exhibit different shrinkage characteristics especially after stretching of the filaments. Such composite filaments may be formed by the extrusion of the two viscous together in side by side relation through each of the orifices of a spinneret mounted in extrusion devices disclosed in United States Letters Patent 2,386,173, patented October 3, 1945.

In accordance with the present invention it has been found that crimped filaments of similar structure can be produced from a single viscose if the filaments are sufficiently small in diameter, being not larger than ten denier per filament. This can be accomplished by extruding the viscose into an aqueous acid coagulating and regenerating bath which has, because of a high total salt content, a rapid dehydrating effect upon the extruded xanthate filaments and sets up therein an at least partially regenerated skin of substantial thickness about a still substantially liquid or exceedingly soft and plastic core. This skin is set up rapidly and, having a strong tendency to shrink as the result of the dehydrating action of the coagulating bath, it apparently expends its circumferential shrinkage component, which is prevented by the incompressible core from exerting a mere reduction in diameter of the filaments, by splitting or rupturing longitudinally of the filaments and then compressing the core, thereby causing part of the core to flow through the rupture, in which state the filaments are finally set up. The portion of the resulting filaments that is forced out of the core responds to the subsequent stretching (which is necessary to obtain the desired crimpliness) differently than the remainder of the filaments, and in this respect, it appears to act as if it had originated from an entirely distinct viscose.

Fig. 1 is an enlarged view of a length of crimped filament, and

Fig. 2 is an enlarged view in cross-section of a bundle of filaments.

The filaments, as shown in the drawing, exhibit in cross-section a structure similar to that heretofore noted when composite filaments are produced from two viscous of widely different age. For example, one portion A of the cross-section has a thick skin showing a break along the juncture with the other portion B which has a thin skin or none at all. As is shown in Figure 1, in the crimped filaments the portion A having the thick skin always takes the inside of the bends of the crimp, because of a stronger tendency to shrink. The skin apparently is composed of slenderer micelles which are more highly oriented than those of the body or core of the filament. It may be differentially dyed by the following procedure: A microscope section of one or more of the filaments mounted in a wax block is taken and mounted on a slide with Meyer's albumin fixative. After dewaxing in xylene, the section is placed in successive baths of 60% and 30% alcohol for a few moments each, and it is then stained in 2% aqueous solution of Victoria Blue BS commercial Dyes of the Dyes of the Dyes, Corp.) for 1 to 2 hours. At this point, the entire section is blue. By rinsing the section first in distilled water and then in one or more baths composed of 10% water and 90% dioxane for a period varying from 5 to 30 minutes depending on the particular filament, the dye is entirely removed from the core, leaving it restricted to the skin areas.

Generally an acid bath having a regenerating capacity equivalent to that of 7 to 14% of sulfuric acid mixed with a small proportion of a zinc salt and a large proportion of sodium sulfate fulfills the requirements of the present invention most satisfactorily. The zinc salt may be zinc sulfate, the coagulating bath containing at least about 0.5% but not more than about 3% thereof. The use of the higher proportion has the advantage of increasing the thickness of skin initially formed, which in turn causes an increase in the differential shrinkage between the two portions of the filaments and results in greater crimpliness. However, it has the disadvantage of increasing the toughness of the skin and making more critical the spinning conditions which will cause rupture to occur consistently. For most purposes it has been found that the most favorable proportion of zinc sulfate is about 1 to 1.5%. The higher proportions between 1.5
to 3% zinc sulfate may be used with entire satisfaction when the higher range of sulfuric acid between 9 and 14% is used, the swelling tendency of the acid on the filaments compensating for the tendency of the zinc salt to form a tough skin.

To assure that the bath exerts a strong dehydration on the filaments, a high proportion of salts, such as sodium sulfate or potassium sulfate between about 13 to 25% or more, should be used.

The viscoses that yield composite-like filaments upon rupture fall within a wide range of types. Generally there may be used viscoses analyzing from 29 to 45% carbon disulfide (based on alpha-cellulose content of pulp), from 7 to 9% of cellulose and from 5 to 9% of sodium hydroxide (based on percent weight in viscosa), and having a common salt (NaCl) test of at least 3 up to 6 or more. The ball fall viscosity is not critical and viscosities having viscosities between 20 and 100 have given satisfactory results. Generally the factors, with the exception of viscosity, are correlated but not strictly. Thus a viscoce containing a proportion of sodium hydroxide in the lower part of the range specified, say from 5 to 7%, may have 9% cellulose and 45% carbon disulfide, but better results are obtained if the proportions of the several factors fall more nearly in corresponding parts (that is, in the higher, lower or intermediate portions) of the several ranges. As stated, this is a general rule to which it is not necessary to adhere strictly. Viscoses which yield the highest degree of crimp in filaments of the type produced in accordance with this invention fall within preferred ranges as follows: 38 to 42% carbon disulfide, 7.5 to 8.5% sodium hydroxide, a common salt test of 4 to 6 and a ball fall viscosity of 40 to 50.

As a general rule it has been found that the optimum results are obtained for any given viscoe by spinning into coagulating baths having from about 8.5% to about 9.5% sulfuric acid, about 1 to 1.5% zinc sulfate, and about 19 to 22% sodium sulfate, with the exception of those viscoses having an extremely high or low proportion of carbon disulfide, with which the best results are obtained with coagulating baths having the higher or lower proportions respectively of sulfuric acid and zinc sulfate.

The coagulating baths should have a temperature between 40° C. and 60° C., preferably 45 to 50° C. The immersion depends on the speed of spinning, and by way of illustration may be between 10 and 90 seconds. The immersion should preferably be sufficient to substantially completely coagulate the filaments before stretching is performed thereon, so that the maximum differential in shrinkage is obtained, the longer immersions resulting in more extensive crimping. Preferably the draw-off speed of the filaments from the spinneret is greater than the velocity of extrusion.

The size of the finished filaments after stretching must not be larger than 10 deniers per filament and preferably is between one and six deniers per filament. For a given set of conditions, the smaller the denier, the greater the crimp. Above about 10 deniers per filament, the crimping is negligible, although the longitudinal rupturing appears to take place.

The longitudinally ruptured filaments must be stretched by at least about 40% (as measured by differential in godet speeds) or its equivalent obtained by tension guides, either of a rotary or stationary type, and the stretching must be followed by relaxation in order to obtain effective crimping. The stage of filament production at which the stretching is effected is not critical, though the most satisfactory results are obtained when the stretching is performed shortly after coagulation while the filaments are still in plastic condition. For example, the filaments after leaving the coagulating bath may proceed in succession about two or more godets, each of which has a greater peripheral speed than that preceding it. The filaments may then proceed through the conventional wet-processing, drying and collecting stages. As they proceed through these stages, they may be manipulated so as to be substantially free of tension, in which event the finished filaments obtained are inherently crumpy. They may, however, proceed through the treatment stages under tension, in which event the final filaments are substantially free of crimp. However, in this latter case they may be readily subjected to tension or for better control of the crimp applied, the greater the crimp obtained, thus providing a means of ready control of the crimp. Stretches of 50 to 80% or more yield excellent crimps. Where necessary the stretching may be facilitated by passage of the filaments through a plasticizing bath, such as of hot water, hot acids, and the like.

The procedure may advantageously be applied to the production of staple fiber as well as continuous or broken filament yarns. An illustrative embodiment of its adaptation to staple fiber production is as follows: The filament bundles proceeding from several spinnerets over stretching godets are combined into tows of 1200 up to 400,000 deniers. The tows while still wet are cut to staple fiber, which is allowed to fall into a liquid bath which may serve merely to effect opening of the fiber clumps and relax the fibers therein, or may also serve the purpose of an additional liquid treatment, such as washing or desulfurizing.

For illustrative purposes, the following specific examples are described:

**Example 1**

A cotton pulp viscoce having 8% by weight sodium hydroxide, 71% by weight cellulose, 40% carbon disulfide (CS₂ based on weight of alpha-cellulose) and a common salt test of 5.5 was
Example 2

A wood pulp viscose otherwise of the constitution of Example 1 and having a common salt point of 4.7 was spun through a 3000 hole spinneret having 3 mil holes into a spinning bath at 45°C containing 9% H2SO4, 1% ZnSO4, and 20% Na2SO4. The filament bundle was stretched 62% between godets but without application of additional plasticizing medium. After collecting and drying in relaxed condition, the final filaments had a size of 1 denier per filament and averaged 15 crimps per inch.

Example 3

A high alpha-cellulose wood pulp was convverted into a viscose having 8% by weight cellulose, 61.5% sodium hydroxide and 33% carbon disulfide (CS2 based on weight of alpha-cellulose) and after aging to a common salt point of 4, was spun through a spinning bath at 50°C containing 7.6% sulfuric acid, 1% zinc sulfate, and 20% sodium sulfate. The speed through the bath was 80 meters per minute and the immersion was 24 inches. The filaments assembled in the form of a tow were given a 65% godet stretch, during which they were plastized with hot water. Shortly after stretching and before any substantial drying of the filaments, they were cut to staple fiber which were immediately allowed to fall into a water bath for wet opening. After processing in conventional manner, the fibers were dried without tension. The resulting fiber had a size of 3 denier per filament and averaged about 12 crimps per inch.

Example 4

A wood pulp viscose of the constitution of Example 1, except that the carbon disulfide was about 43%, was spun at an age of about 5% common salt point into a spinning bath at 45°C containing 12% sulfuric acid, 1% zinc sulfate, and 20% sodium sulfate. After leaving the bath, the filaments were given a 65% godet stretch. After wet processing, the filaments were dried in a relaxed condition to give a product having a size of 3 denier per filament and averaging 8 crimps per inch.

Example 5

A cotton pulp viscose having the constitution of that of Example 1 (except that the carbon disulfide was 43%), was spun, after aging to a common salt point of about 4%, into a bath at 45°C containing 9% sulfuric acid, 0.5% zinc sulfate, and 20% sodium sulfate. The filaments, after leaving the bath, were given a godet stretch of 60%. After wet processing, the filaments were dried in relaxed condition. The product had a size of 3 denier per filament and averaged 13 crimps per inch.

Example 6

A wood pulp viscose otherwise of the constitution of Example 1 was spun, after aging to a common salt point of 5.2, into a bath at 45°C containing 9% sulfuric acid, 1.5% zinc sulfate, and 20% sodium sulfate. The speed through the bath was 80 meters per minute and immersion was 54 inches. The filaments, after leaving the bath, were given a 70% godet stretch. After wet processing, the filaments were dried in relaxed condition. The filaments obtained had a size of 5 denier per filament, and averaged 15 crimps per inch. The filaments had a tensile strength of 2.11 grams per denier dry and 1.13 grams per denier wet, and had extensibilities of 15.9% dry and 16.3% wet.

Example 7

The procedure of Example 6 was followed, except that no godet stretch was applied, and the filaments were dried under slight tension, so that no crimp was obtained in the product. Subsequently the filaments were soaked with cold water, stretched 45%, allowed to relax and dried in relaxed condition. The resulting product exhibited an average of 10 crimps per inch.

Example 8

A wood pulp viscose having 8% by weight of sodium hydroxide, 8% cellulose, 33% carbon disulfide (CS2) based on alpha-cellulose) and aged to a common salt point of 3.5 was spun into a bath at 45°C containing 11% sulfuric acid, 1% zinc sulfate, and 20% sodium sulfate. An immersion of 24 inches and a speed of 80 meters per minute were used. After leaving the bath, the filaments were plastized with hot water and given a godet stretch of 65%. Shortly after stretching and before any substantial drying of the filaments, they were cut to staple fibers, which were immediately wet opened and processed in conventional manner, until finally dried without tension. The resulting fibers had a size of 2 denier per filament, and averaged 10 crimpes per inch.

Example 9

A viscose of the constitution of Example 5 was spun into a bath at 45°C, containing 9% sulfuric acid, 3% zinc sulfate and 20% sodium sulfate. An immersion of 74 inches and a speed of 60 meters per minute were employed. After leaving the bath, the filaments were given a 60% godet stretch. After wet processing, the filaments were dried in relaxed condition. The resulting product had a size of 2½ denier per filament, and averaged 11 crimpes per inch.

The resulting filaments which have dry tensile strengths up to about 2¼ to 2½ or more grams per denier, wet tensile up to about 1 to 1½ or more grams per denier and dry extensibilities down to as low as about 15%, may have from about 5 up to 30 or more crimpes per inch.

The individual filaments produced in accordance with this invention have a structure having a cross-section at all points of the filament length which comprises two more or less distinct component areas side by side, each of which appears to have a different construction or state of physical aggregation than that of the other. The distinct areas exhibit therein differences in shrinkage, swelling, extensibilities, strength, orientations, dye absorptions, chemical reactivity, hydrophilic and hydrophobic properties, and they show different skin thicknesses which is readily observable as a differenc-
The crimped filament takes the form of a regular or irregular helical coil which may reverse its direction at more or less frequent intervals of regular or irregular occurrence, the eccentric components of the filament following a helical path about the longitudinal axis of the filament, which path may reverse itself at more or less frequent intervals or regular intervals. Thus, a three-dimensional crimp with the crimps out of phase is present in the filament.

The individual filaments produced in accordance with this invention, in their state of normalcy are characterized by a stabilized condition having an inherent distortion which imparts a permanently recoverable crimp. The only condition under which it loses its crimp (and in this case the loss is temporary) is that prevailing when the crimped filament is wetted and caused to dry while under tension. It can be repeatedly wetted and dried without an appreciable loss in crimpiness, as long as it is permitted to dry in a relaxed condition. If dried under tension the crimp can be recovered merely by wetting and drying while relaxed.

No completely satisfactory tests have been devised to evaluate the degree of permanency of a crimp. However, the crimped filaments of this invention have been found to possess a "crimp retentivity" ranging from about 60% up to a value approaching 100% when tested in accordance with the procedure outlined in the Hardy et al. Patent 2,287,099, issued June 23, 1942. Individual filaments when subjected to that test, not merely after a single immersion but after as many as 20 or more immersions have been found to show crimp retentivities as high as substantially 100%, and relatively few of the filaments made in accordance with this invention have been found to have crimp retentivities as low as 60%. The crimp retentivity test as outlined in Patent 2,287,099 is performed in water at 60°C. It has been found that for the filaments of this invention, crimp retentivity is fully as high when cold or boiling water is used in the test. Thus, the filaments of the present invention show up just as well, and about 60 to 100%, when measured by the "crimp recovery from stretch" test outlined in the above mentioned Patent 2,287,099, as they do when they are evaluated by the crimp retentivity test.

The filaments and staple fibers of the present invention do not appreciably lose their crimp during the ordinary conditions of wear, in either of which temperatures ranging from the neighborhood of the freezing point and the boiling point of water are encountered. Fabricated products made from these filaments and fibers thus have properties which may be used to approach those of natural wool in some respects.

The relative size of the distinct areas may be varied widely. Preferably the component having a thin skin or no skin amounts to about 1/4 to 1/5 direction of more or less frequent intervals, though proportions as low as about 15% and as high as 75% may be used for special purposes. The thick skin may correspondingly occupy from about 25 to 90% of the filament circumference.

The crimped filaments and fibers of this invention show improved spinning quality, increased bulk resilience, and a fabric appearance and feel that approaches that of wool.

We claim:

1. A regenerated cellulose filament having a generally helical crimp, said filament having a thick skin constituting only a portion of the periphery thereof, another peripheral portion thereof having a skin of relatively thin to negligible thickness, the thick-skinned portion being positioned at the inside of the bends of the crimp.

2. A regenerated cellulose filament having a generally helical crimp, said filament having a thick skin constituting only a portion of the periphery thereof, another peripheral portion thereof having a skin of relatively thin to negligible thickness, the thick-skinned portion being positioned at the inside of the bends of the crimp, and improved Spinning quality, increased bulk resilience, and a fabric appearance and feel that approaches that of wool.

3. A regenerated cellulose filament having a generally helical crimp, said filament having a thick skin constituting only a portion of the periphery thereof, another peripheral portion thereof having a skin of relatively thin to negligible thickness, the thick-skinned portion being positioned at the inside of the bends of the crimp, and having a dry tensile strength of at least 31/4 to 23/16 grams per denier and a wet tensile strength of at least 1 to 11/4 grams per denier.

4. A regenerated cellulose filament having a generally helical crimp, said filament having a thick skin constituting only a portion of the periphery thereof, another peripheral portion thereof having a skin of relatively thin to negligible thickness, the thick-skinned portion being positioned at the inside of the bends of the crimp, and having a dry tensile strength of at least 31/4 to 23/16 grams per denier.

5. A dry regenerated cellulose filament having portions thereof under different internal strains giving rise to inherently and permanently different shrinkage characteristics said filament having a thick skin constituting only a portion of the periphery thereof and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

6. A dry substantially straight artificial filament of regenerated cellulose having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped on being treated with water said filament having a thick skin constituting only a portion of the periphery thereof, and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

7. A dry substantially straight regenerated cellulose filament under internal strains giving rise to different shrinkage characteristics and a consequent potential capacity to become crimped on being treated with water said filament having a thick skin constituting only a portion of the periphery thereof and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

8. A dry artificially regenerated cellulose, said filament upon having its crimp removed by stretching, having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated in the relaxed state with water, said filament having a thick skin constituting only a portion of the periphery thereof and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

9. A dry artificially regenerated cellulose, having a denier of from 1 to 10, said
filament upon having its crimp removed by stretching, having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated in the relaxed state with water, said filament having a thick skin constituting only a portion of the periphery thereof and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

10. A dried crimped artificial filament of regenerated cellulose, said filament upon having its crimp removed by stretching, having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated in the relaxed state with water, said filament having a thick skin constituting only a portion of the periphery thereof and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

11. A dry crimped artificial filament of regenerated cellulose having a denier of from 1 to 10, said filament upon having its crimp removed by stretching, having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated in the relaxed state with water, said filament having a thick skin constituting only a portion of the periphery thereof and having another peripheral portion thereof provided with a skin of relatively thin to negligible thickness.

12. A dry substantially straight artificial filament of regenerated cellulose substantially as shown and described having a denier of from 1 to 10 and having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated with water, said filament having a core within a periphery consisting of two distinct portions of substantial extent, one portion having a thick skin and extending around one side of the core, and the other portion extending around the other side of the core having a skin of relatively thin to negligible thickness joined at its ends to the ends of said thick skin.

13. A dry substantially straight artificial filament of regenerated cellulose substantially as shown and described having a denier of from 1 to 10 and having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated with water, said filament having a core within a periphery consisting of two distinct portions, each constituting at least one fourth of the entire filament periphery, one portion having a thick skin and extending around one side of the core, and the other portion extending around the other side of the core having a skin of relative thin to negligible thickness joined at its ends to the ends of said thick skin.

14. A crimped artificial filament of regenerated cellulose substantially as shown and described having a denier of from 1 to 10, said filament upon removal of its crimp by drying in stretched condition having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated in the relaxed state with water, said filament having a core within a periphery consisting of two distinct portions of substantial extent, one portion having a thick skin and extending around one side of the core, the other portion extending around the other side of the core having a skin of relatively thin to negligible thickness joined at its ends to the ends of said thick skin, the thick skin being at the inside of all bends of the crimped filament.

15. A crimped artificial filament of regenerated cellulose substantially as shown and described having a denier of from 1 to 10, said filament after removal of its crimp by drying in stretched condition having unbalanced internal strains giving rise to different shrinkage characteristics and the potential capacity to become crimped upon being treated in the relaxed state with water, said filament having a core within a periphery consisting of two distinct portions, each constituting at least one fourth of the entire filament periphery, one portion having a thick skin and extending around one side of the core, the other portion extending around the other side of the core having a skin of relatively thin to negligible thickness joined at its ends to the ends of said thick skin.
being treated in the relaxed state with water, said filament having a core within a periphery consisting of two distinct portions, each constituting at least one fourth of the entire filament periphery, one portion of the periphery having a thick skin and extending around one side of the core, the other portion of the periphery extending around the other side of the core, having no skin and being joined at its ends to the ends of said thick skin, the thick skin being at the inside of all bends of the crimped filament.

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