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STRETCH-SPUN REGENERATED CELLULOSE
FIBER HAVING AN IMPROVED LOOP
TENACITY

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This invention relates to an improved viscose composition, and to regenerated cellulose fibers, filaments and yarns produced from such an improved viscose composition. More particularly, it relates to regenerated cellulose fibers, filaments and yarns having a high dry tenacity (a dry tenacity in excess of 2.5 grams per denier), and having an improved ratio of loop tenacity to dry tenacity.

In the absence of a specific statement to the contrary, the term "tenacity" as used throughout the specification and claims shall refer to the dry tenacity of fibers, filaments and yarns.

The "loop tenacity" of a yarn is the breaking tenacity of yarn determined in the following manner: Two pieces of yarn are used; both ends of one piece are clamped in one jaw of a testing machine, the other piece is passed halfway through the loop formed by the first piece and the ends brought together and clamped in the other jaw of the testing machine. As the jaws are moved apart, one of the pieces of yarn breaks at the point of contact with the other piece. The force required to break the yarn in this manner is its "loop tenacity."

It has been long known that the stretch-spinning, from viscose, of regenerated cellulose fibers and filaments will cause the cellulose molecules in those structures to orient themselves in the direction of the fiber axis. The more pronounced the degree of orientation of the molecule, the higher is the tenacity of the resulting fiber or filament.

Unfortunately, increased molecular orientation also tends to produce more brittle structures. The increase in brittleness of fibers, the molecules of which are highly oriented along the fiber axis, may, in certain cases, become so serious as to interfere with the commercial usefulness of these fibers.

It is therefore an object of the present invention to prepare an improved viscose composition from which fibers and filaments may be stretch-spun with a high degree of molecular orientation in the direction of the fiber axis and in which the resulting fibers or filaments will not be unduly brittle.

It is another object of the present invention to incorporate in a viscose solution a modifying agent which will reduce brittleness of fibers or filaments which are stretch-spun from the said viscose.

It is a further object of the present invention to provide an improved process for the stretch-spinning of regenerated cellulose filaments and

fibers from viscose solutions for the production of high tenacity filaments and fibers.

Other objects of the invention will appear hereinafter.

The objects of the invention may be accomplished, in general, by incorporating a modifying agent in a viscose composition, which modifying agent will have the property of reducing the brittleness of fibers and filaments spun from said composition under a high degree of stretch. The viscose modifying agent of the present invention is a nitrogen-unsubstituted sulfonamide containing more than ten carbon atoms, at least four of which are in a straight chain. Particularly desirable results have been obtained by the use of sulfonamides derived from petroleum hydrocarbons or normal alkanes by treatment with sulfur dioxide and chlorine and subsequent conversion of the sulfonyl chlorides to sulfonamides in the manner described in U. S. Patent No. 2,174,507 and U. S. Patent No. 2,197,800. In addition to sulfonamides derived from long chain aliphatic hydrocarbons, nitrogen-unsubstituted sulfonamides made from aralkyl compounds in which the alkyl portion contains at least four carbon atoms, for example, amylbenzene or diamylbenzene sulfonamide, may also be used. Sulfonamides containing less than ten carbon atoms or having less than four carbon atoms in a straight chain, such as sulfonamides derived from toluene, are not effective. The viscose modifiers used in accordance with the present invention are all soft, waxy, or oily materials insoluble in water or acids, but either soluble or readily dispersible to a semi-colloidal state in a viscose composition.

The following detailed examples are submitted for purposes of illustration of the specific steps which may be used in practicing the present invention. These examples are not, of course, to be taken as limitative of the present invention.

Example I

Viscose prepared from cotton linters cellulose and containing 7% cellulose and 6% alkali is modified by dispersing in it 2% (based on the weight of the cellulose) of a sulfonamide derived from petroleum white oil, for example, by the process of U. S. Patent No. 2,174,507. The modified viscose is allowed to ripen to a salt index of 5.0 and is spun into thread (150 denier—40 filament) by extruding the viscose through a spinneret having holes 0.003 inch in diameter into a coagulating and regenerating bath containing 11% H_2SO_4 , 23% Na_2SO_4 , 4% glucose, and 0.85% ZnSO_4 . The apparatus and general pro-

cedure used to form these threads are similar to those described in U. S. Patent No. 2,083,252. The thread is caused to travel approximately 180 inches through the acid bath by passing around freely rotating horizontal rollers, some of which either have slots in them or vanes extending from their under-sides, and then around one vertical roller before being wound upon a bobbin. It is the purpose of the rollers located in the bath to build up a uniform tension on the thread and thus orient the cellulose structure. The tension built up in this manner on the gel thread is in this case approximately 0.85 gram per denier. Other conditions included in the spinning process are a temperature of 55° C. in the spinning bath and a wind-up speed on the bobbin of 3,500 inches per minute. After removing the thread from the spinning machine, it is washed with water and allowed to dry under tension on the bobbin. Tests made to determine the physical properties of this thread show that it has a dry tensile strength in excess of 3.0 grams per denier with a ratio of loop tenacity to dry tenacity 10%–15% higher than is generally obtained in control yarn spun under exactly similar conditions except for the presence of the long-chain sulfonamide in the viscose.

Example II

Cotton linters viscose, containing 7% cellulose and 6% alkali, is modified with 10% (based on the weight of the cellulose) of a sulfonamide derived from cetane. This modifier, although incompletely soluble in the viscose, is readily dispersed by vigorous mechanical mixing to form a semi-colloidal suspension throughout the viscose. The modified viscose is spun at an index of 3.7 into a coagulating and regenerating bath comprising 9% H₂SO₄, 19% Na₂SO₄, 4% glucose, and 0.85% ZnSO₄. Tension on the spinning thread is 0.35 gram per denier, the bath travel is 130 inches, the bath temperature is 45° C. and the spinning speed is 2,500 inches per minute. The thread obtained in this experiment is extremely soft and free from brittleness, as characterized by a high ratio (85%) of loop tenacity to dry tenacity. Control yarn had a ratio of loop to dry tenacity of 75%.

Example III

Viscose derived from wood pulp, but still containing 7% cellulose and 6% alkali, is modified with 2% (based on the weight of the cellulose) of the sulfonamide used in Example I. Modified viscose is spun into highly oriented threads in a manner similar to that used in Example I. These threads are also similar in properties to those of Example I.

Example IV

Cotton linters viscose is modified by dispersing in it 2% (based on the weight of the cellulose) of amylbenzene sulfonamide obtained by treating amylbenzene with chlorosulfonic acid and reacting the product with ammonia. This viscose is spun into high tenacity thread using essentially the same technique as in Example I except that the coagulating and regenerating bath contains 9% H₂SO₄, 23% Na₂SO₄, 4% glucose, and 0.85% ZnSO₄, and the spinning tension is 0.66 gram per denier. The resulting fibers have a tenacity of about 3 grams per denier and a loop tenacity 5%–10% better than controls.

Example V

Diamylbenzene sulfonamide made from di-

amylbenzene in the same manner as the mono-amyl compound described in Example IV (2% based on the weight of the cellulose) is added to cotton linters viscose of the same composition as that used in Example I. The modified viscose is spun into a bath of composition similar to that in Example I, but the temperature in the spinning bath is 45° C. and the spinning speed 2,500 inches per minute. Yarn obtained in this experiment is strong, almost as soft as in Example I, and shows a characteristic improvement of about 5% in loop strength over controls.

Example VI

Viscose modified in a similar manner to that of Example I is spun into a regenerating bath comprising 9% H₂SO₄, 23% Na₂SO₄, 4% glucose, and 0.85% ZnSO₄, using a bath travel of 27 inches (only one roller) and a tension on the gel thread of 0.13 gram per denier. The thread after winding on the bobbin is washed and dried and then shows a loop tenacity which is better than 95% of the dry strength as against a normal of 85%–90% for control thread.

The sulfonamides operable according to this invention are compounds of the formula R—SO₂NH₂, wherein R is an organic radical containing more than ten carbon atoms, at least four of which are in a straight aliphatic chain. R may, therefore, be alkyl (straight chain or forked chain), aralkyl or alkyl-cycloalkyl. It may contain inert substituents; i. e., substituents which are chemically substantially inert toward the viscose under the conditions of the process; e. g., chloro, hydroxyl, nitro groups, etc. In fact, the sulfonamides obtained according to the process of U. S. Patents Nos. 2,174,507 and 2,197,800 usually contain small proportions of chlorine as substituents. Among the sulfonamides coming within the scope of the invention may be mentioned n-dodecanesulfonamide, n-pentadecanesulfonamide, n-hexadecanesulfonamide, n-octadecanesulfonamide, hexylbenzenesulfonamide, dodecylbenzenesulfonamide, amylcyclohexanesulfonamide, decylcyclohexanesulfonamide, amylchlorobenzenesulfonamide, hexylnitrobenzenesulfonamide, and polysulfonamides such as 1,12-dedecanedisulfonamide or 1,14-tetradecanedisulfonamide. Mixed sulfonamides, for example, those obtained by treating crude hydrocarbons or mixed hydrocarbons with sulfur dioxide and chlorine and reacting the product with ammonia may be used advantageously.

Although the quantity of viscose-modifying agent to be added to the viscose composition may vary between wide limits, it is preferred that not more than 10% of the modifier (based on the weight of the cellulose) be used, since addition of a sulfonamide in excess of that proportion tends to lower unduly the strength of the fibers. The best results; i. e., combination of reduced brittleness with great tenacity, are obtained when the modifying agent is used in proportions of 1% to 5% (based on the weight of the cellulose). Proportions of modifier lower than 1% do not, in general, produce very marked improvements. For these reasons, the preferred range is 1% to 5% of the modifier (based on the weight of the cellulose) in the viscose. In mixing the modifying agent with the viscose composition, it is highly desirable that an efficient mechanical mixing device be used.

The viscose used in the preparation of fibers and filaments according to the present invention

may be made from any suitable cellulose material, for example, cotton linters or wood pulp, or mixtures of the two. The modified viscose may be aged to a salt index of between 3 and 8. The viscose may also vary from 7% to 10% in cellulose content and from 4% to 8% in alkali content.

The viscose may also contain other modifying agents so long as they do not have any unfavorable influence on the sulfonamide modifying agent of the present invention.

The viscose may be spun into any suitable coagulating and regenerating bath. The composition of the coagulating and regenerating bath will, of course, vary with the composition of the viscose. Any coagulating and regenerating baths which may be used for the stretch-spinning of regenerated cellulose filaments from viscose are considered to be within the scope of the present invention. For example, coagulating and regenerating baths comprising between 6% and 15% sulfuric acid, 19%–25% sodium sulfate, 0.1%–1% glucose, and 0.5%–1% zinc sulfate will be suitable for use in accordance with the present invention.

It is immaterial whether the spinning operation is carried out by the bobbin spinning process or the bucket spinning process. It is, however, important that regardless of the process used in the spinning of filaments and yarns, in accordance with the present invention, the yarn must be submitted to considerable tensions over a bath travel of at least 15 to 30 inches and preferably between 100 and 250 inches. Any process in which the thread is stretched during the coagulating and regenerating thereof will be suitable for use in accordance with the present invention. For example, the process outlined in the U. S. Patent No. 2,083,252 to Bradshaw and Hoff is particularly suitable for obtaining high tenacity threads of reduced brittleness. The size of the yarn spun, or the number of filaments in the yarn spun, is immaterial. After spinning, the regenerated cellulose fibers, filaments, and yarns may be washed free of acid and dried. Such yarns are preferably not desulfured or bleached by submitting the same to treatment with alkaline agents since under these conditions at least part of the sulfonamide modifiers will be removed from the yarn.

The yarns produced in accordance with the present invention, since they are generally undesulfured and unbleached, will have particular utility in the manufacture of tire cords, balloon fabrics and sail cloth.

The modified viscose solutions of the present invention, when stretch-spun in the production of high tenacity filaments and fibers by known procedures, will produce filaments and fibers of a reduced brittleness or, as above described, an increased ratio of loop tenacity to dry tenacity.

Inasmuch as many modifications and changes may 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 such details except as set forth in the appended claims.

We claim:

1. A viscose composition containing incorporated therein a nitrogen-unsubstituted sulfonamide containing more than ten carbon atoms at least four of which are in a straight chain.

2. A viscose composition containing incorporated therein 1%–5% (based on the weight of the cellulose in the viscose) of a nitrogen-unsubstituted sulfonamide containing more than ten carbon atoms at least four of which are in a straight chain.

3. A viscose filament-forming composition containing incorporated therein a compound of the formula $R-SO_2NH_2$ wherein R is an organic radical containing more than ten carbon atoms at least four of which are in a straight chain.

4. A viscose filament-forming composition containing incorporated therein a compound of the formula $R-SO_2NH_2$ wherein R is an aliphatic radical containing more than ten carbon atoms at least four of which are in a straight chain.

5. A viscose filament-forming composition containing incorporated therein a compound of the formula $R-SO_2NH_2$ wherein R is an aralkyl radical containing more than ten carbon atoms and in which the alkyl portion of the molecule contains at least four carbon atoms in a straight chain.

6. Regenerated cellulose filaments containing incorporated therein a nitrogen-unsubstituted sulfonamide containing more than ten carbon atoms at least four of which are in a straight chain.

7. Regenerated cellulose filaments containing incorporated therein 1% to 5% of a nitrogen-unsubstituted sulfonamide containing more than ten carbon atoms at least four of which are in a straight chain.

8. Regenerated cellulose filaments containing incorporated therein a compound of the formula $R-SO_2NH_2$ wherein R is an organic radical containing more than ten carbon atoms at least four of which are in a straight chain.

9. Regenerated cellulose filaments containing incorporated therein a compound of the formula $R-SO_2NH_2$ wherein R is an aliphatic radical containing more than ten carbon atoms at least four of which are in a straight chain.

10. Regenerated cellulose filaments containing incorporated therein a compound of the formula $R-SO_2NH_2$ wherein R is an aralkyl radical containing more than ten carbon atoms and in which the alkyl portion of the molecule contains at least four carbon atoms in a straight chain.

11. A viscose filament-forming composition containing incorporated therein a petroleum white oil sulfonamide.

12. A viscose filament-forming composition containing incorporated therein cetane sulfonamide.

13. A viscose filament-forming composition containing incorporated therein diamylbenzene sulfonamide.

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