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2,958,569

PRODUCTION OF THREADS AND OTHER SHAPED OBJECTS FROM VISCOSE

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8 Claims. (Cl. 18—54)

This invention relates to a process for the manufacture of fibers, threads, foils, films and other shaped objects by spinning viscose in acid spinbaths, and preferably spinbaths containing sulphuric acid, in such manner as to confer upon the resulting products certain improved properties as hereinafter described. The invention also relates to the resulting improved products.

One of the principal objects of the present invention is to provide a new and improved method for spinning artificial products such as threads and other shaped objects from viscose in such manner as to confer upon them greatly improved properties as regards their strength and elasticity. A further object of the invention is to provide a new and improved method for producing products of the kind just indicated having unusually strong and well-defined peripheral zones, i.e., the so-called skin structure or effect mentioned above. A still further object of the invention is to provide improved products of the kind indicated.

The manner in which these and other objects and features of the invention are attained will appear more fully from the following description thereof, in which reference is made to typical and preferred procedures in order to indicate more fully the nature of the invention, but without intending to limit the invention thereby.

In Belgian Patent No. 509,499 conditions are described whereby under special circumstances in the manufacture of formed products from viscose, such as fibers, threads, foils, films and the like, the so-called skin effect or skin structure throughout the total cross section of those products may be obtained. This means that throughout the total cross section of such products the gel structure is of the same type as that which in normal products from viscose is indicated as the known so-called skin structure. In this Belgian patent it is recognized as essential for the forming of the desired skin structure that as soon as the pH-value in the coagulating thread during the spinning operation is diminished to 7 or lower, there must be present zinc ions which may form cross links between the cellulose xanthate molecules so that a special molecular net structure will be brought about. According to the Belgian patent it is only possible to obtain at each point of the spinning thread the presence of zinc ions for the net formation active condition if the viscose is free from sodium trithiocarbonate. This peculiar net structure of the cellulose xanthate gel was considered to be different from the structure obtained in the absence of zinc, and also different from the structure which may be formed in the presence of both zinc and sodium trithiocarbonate.

According to the present invention a process is provided by which it is made possible to use viscose containing sodium trithiocarbonate and yet obtain the typical skin structure in the spun viscose product such as thread or other shaped object.

The process according to the present invention is characterized in that there is employed a viscose which contains certain organic substances which are soluble in

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viscose and which form with the zinc in the spinning product temporarily stable zinc chelates, said viscose being spun in a zinc-containing spinbath and the freshly spun products being subjected to stretching.

It was discovered that it was possible in this manner to bind first the zinc ions penetrating from the spinbath in the spinning product as an organic zinc chelate, whereby said zinc chelate remains stable while the coagulation proceeds further, from the outside to the inside of the formed product until the pH locally has diminished to about 7 or lower, after which the organic zinc chelate decomposes in such a manner that the zinc ions serve as link formers between the cellulose xanthate molecules.

The nature of the particular chelating substances which are mentioned hereinafter may be described as follows (see Chemistry of the Metal Chelate Compounds, Martell and Calvin, New York, 1952/53, page 1);

"When a metal ion combines with an electron donor, the resulting substance is said to be a complex, or coordination compound.

"If the substance which combines with the metal contains two or more donor groups so that one or more rings are formed, the resulting structure is said to be a chelate compound, or metal chelate, and the donor is said to be a chelating agent."

According to an earlier description chelating agents, or as they will be called here, chelate formers, are molecules which contain at the same time two or more atom groups each having available a main valency or a sub-valency by which said atom groups may retain between them a metal ion, in the present case therefore a zinc ion, in the manner as indicated by the Greek word "chela" (in the manner of a claw or a pair of tongs) with binding forces at two or more sides. These binding forces emanate especially from atoms such as N, S and sometimes also O. It is also possible to consider the chelates involved in the process according to the present invention as a kind of "interior (or internal) metal complex salt."

According to the present invention the viscose employed for spinning contains certain organic chelate forming substances or classes of substances, i.e., substances which at the instant of formation of the product, e.g. a fiber or a thread or a foil, form with zinc temporarily a zinc chelate. Not all existing or known chelate formers are suitable for use in the process according to the present invention, however, since they have to comply with certain requirements set forth hereinafter. Consequently, only those substances or classes of substances listed hereinafter are contemplated as falling within the scope of the present invention.

To be suitable for use in accordance herewith, the chelate formers must be at least slightly soluble in the viscose, since it has been found that the chelate formers can only give the desired effect in solubilized condition. Furthermore, the zinc chelate formed by the chelate former and the zinc must have a certain restricted or limited stability. This stability must be such that the zinc chelate is stable at a higher pH so that the chelate formers can perform their specific chelate function under the circumstances mentioned. On the other hand, they must become unstable as the pH lowers during the formation of the product so that they may at the right moment release or give up the zinc ion so as to perform its function as link former between the cellulose xanthate molecules.

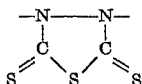
Spinning is always done in zinc-containing acid spinbaths, and preferably spinbaths containing sulphuric acid. These baths may also at the same time contain other known spinbath additives such as sodium sulphate, magnesium sulphate and the like salts.

To obtain good strength in the viscose product a

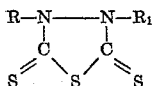
more or less extensive stretching of the freshly spun product is always necessary. The greater the stretch, the greater is the strength obtained thereby. Stretching to a relatively great extent may be done in a so-called one-bath process as well as in a two-bath process.

Experiments have shown that very satisfactory chelate-forming substances or classes of substances useful for carrying out the processes according to the present invention include the following:

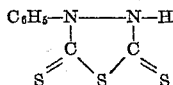
- a. Organic compounds having the thiazole nucleus; e.g., thiazole derivatives such as mercaptobenzothiazole.
- b. Organic compounds having the imidazole nucleus, e.g., imidazole derivatives such as mercapto-benzimidazole.
- c. Organic xanthic acids and their alkali metal salts, especially the sodium salts, e.g., sodium-n-amyloxanthate.
- d. Organic compounds having the nucleus



and more particularly one or more compounds of the formula



where R and R₁ represent a substituted or non-substituted aryl radical, a substituted or non-substituted alkyl radical, or hydrogen. As further examples of such compounds there may be mentioned 5-mercapto-3-phenyl-2-thio-1,3,4-thiadiazolon-2. Formula:



and similar compounds in which the phenyl radical is replaced by a halophenyl, a cyclohexyl, or an amyl radical, respectively.

e. Organic compounds having an OH-radical participating in chelate formation, said OH-radical having an acidic character, and preferably occupying a position in the molecule relatively close to a second radical having an active main valency or subvalency capable of coacting with said OH-radical in chelate formation; e.g., 8-oxyquinoline.

As to the (e) subclass of compounds, it may be noted that alcoholic OH-radicals (dissociation constant 10⁻¹⁶) are not active; phenolic OH-radicals (dissociation constant 10⁻⁹) are in contrast thereto very active when used according to the invention. Due to the higher dissociation constant a phenolic OH-radical has in the alkaline medium of the viscose much stronger electron donor properties than an alcoholic OH-radical.

The amount of the foregoing chelate-forming substances to be employed in the viscose may be very small, relatively speaking. In some cases about 0.05% and less, based on the weight of the viscose, was found to be sufficient to obtain the desired effect. It is, however, also possible to employ larger proportions of the chelate-forming substances, say up to 1% or more by weight of the viscose.

It has been discovered that in the process according to the present invention the best results are obtained if e.g. the sulphuric acid content of the spinning bath, the zinc sulphate content of the spinning bath, and the alkali content of the viscose are as much as possible adjusted relatively to each other.

It is preferred to adjust the zinc content of the spinning bath to at least 2-3% by weight of zinc sulphate, since at lower concentrations of the zinc sulphate the physical properties of the products are generally somewhat less satisfactory. Generally speaking, spun viscose products with especially good properties are obtained when the

sulphuric acid content of the spinning bath, expressed in percent by weight, is at least about 0.8 times the alkali content of the viscose, also expressed in percent by weight; however, the value 1.3 times the alkali content of the viscose should not be notably exceeded for the sulphuric acid content of the spinbath.

The skin structure which the spun products obtained according to the process of the present invention show in cross section, and which is to a great extent uniform throughout the total cross section, is always accompanied by especially favorable physical properties such as high break strength, high double-loop strength and also high abrasion resistance, whereas the swelling power in water is small. The wet strength is high relative to the dry strength.

In order to indicate still more fully the nature of the present invention, the following examples of typical procedures are set forth, it being understood that these are presented by way of illustration only, and not as limiting the scope of the invention. Percentages here and elsewhere are by weight unless the context indicates otherwise.

Example I

A viscose with a cellulose content of 8.4% and an alkali content of 4.8% was prepared by xanthating with 33% CS₂, based on the cellulose. 0.15% 2-mercaptobenzothiazole, based on the viscose, was incorporated therein. The thus-treated viscose was spun with a xanthate ratio of 0.50, a viscosity of 35 sec. (falling-ball test), and a ripeness of 12° Hottenroth. The spinning bath had the following composition: 4% H₂SO₄, 18% Na₂SO₄, 4% ZnSO₄, and the remainder water. The temperature of the spinning bath was 50° C. and the immersion stretch amounted to 40 cm. After a stretch of 75% the final draw-off speed amounted to 35 m./min. The finished thread contained 200 filaments and had a total titre of 400 denier.

A thread was obtained with a good skin structure and a swelling capacity of only 75%. The product was characterized by a good abrasion resistance while the bending strength and the double-loop strength were also very good. The mechanical properties were as follows: dry strength 270 g./100 denier, dry elongation 20%, wet strength 142 g./100 denier, wet elongation 35%.

Example II

In the preparation of a viscose with a 7.3% cellulose content and a 6.8% alkali content, 8-oxyquinoline in the amount of 0.1%, calculated on the viscose, was added to the alkali cellulose after which the alkali cellulose was xanthated with 36% CS₂. The resulting viscose was spun with a xanthate ratio of 0.48, a ripeness of 22° Hottenroth, and a viscosity of 60 sec. (falling-ball test) according to the two-bath spinning method. The first bath had a temperature of 70° C. and an immersion stretch of 120 cm. was used. The composition of the first bath was 8% H₂SO₄, 19% Na₂SO₄, 6% ZnSO₄, and the remainder water. The second bath had a temperature of 90° C. and consisted of spin bath diluted to a H₂SO₄ concentration of 1.5%. The stretch was 110% and the final draw-off speed 70 m./min.

A thread was spun of 1150 denier with 660 filaments and having excellent physical properties. The swelling in water was 70% and both the double-loop strength and abrasion resistance were very good. The dry strength amounted to 401 g./100 denier, the dry elongation 23.4%, the wet strength 310 g./100 denier, and the wet elongation 28%. The fatigue resistance of a tire cord manufactured from this thread was very good.

Example III

The same procedure was followed as in Example I with the exception that instead of 2-mercapto-benzothiazole the viscose contained 0.2% Na-n-amyloxanthate. The thread thereby obtained had a swelling capacity of

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80% with a good skin structure. The dry strength amounted to 290 g./100 denier, the dry elongation 21%, the wet strength 148 g./100 denier, and the wet elongation 43%.

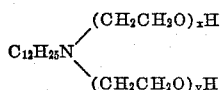
Example IV

A viscose having a cellulose content of 7.7% and an alkali content of 5.5%, and which contained 0.1% of 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolon-2 (calculated on the viscose), was spun at a xanthate ratio of 0.52; a viscosity of 57 sec. (falling-ball test), and a Hottenroth ripeness of 19.5° according to the two-bath process while being stretched by 90%. The final collecting speed amounted to 60 m./min. A thread of 1840 denier and having 1000 filaments was obtained. The first bath contained 6% of H_2SO_4 , 17.8% of Na_2SO_4 and 3.8% of ZnSO_4 . The temperature of this bath amounted to 60° C. The second bath contained 2% of H_2SO_4 and had a temperature of 90°. The threads obtained showed a good skin structure. The swelling in water amounted to 70%. The double-loop strength, the resistance to abrasion, and the fatigue resistance of a tire cord made from this yarn were very good. The dry strength was 4 g./denier at a dry stretch of 23%.

Frequently it is not feasible to spin viscoses to which the chelate-forming substances according to the present invention are added, at such high speeds as unmixed viscoses. The number of thread ruptures occurring with such additions increases at speeds quite feasible with unmixed viscoses to an unacceptable magnitude. However, it has been found that when this difficulty occurs it may be largely overcome by spinning in the presence of surface active substances. In addition thereto or instead thereof tubes arranged in the spinbath may be used, these tubes consisting of portions of different diameter through which the freshly spun threads are guided. These tubes, which are arranged with the narrowest part closest to the spinneret, reduce the tensions exercised on the threads in the vicinity of the spinneret. Applying both steps renders it possible to approach spinning speeds possible for unmixed viscoses.

When surface active substances are employed, they may be added either to the viscose or to the spinning bath, or to both. They may be of the anion-active, cation-active or non-ionic type.

As examples of suitable surface-active substances may be mentioned: praestab oil, lauryl triethyl ammonium-chloride and the polyethylene oxide derivative on the market under the name of Hüls V 1011 T, which has the structure:



where $x+y=11$ to 12, this compound being similar to Armour & Company's Ethomeen C25 where $x+y=15$.

The surface active substances may be added to the viscose in various proportions such as 0.2–0.6, 0.2–0.75 and 0.1–1% by weight, respectively, based on the cellulose in the viscose, and lauryl pyridiniumchloride, the latter being added to the spinbath in proportions of 20–100 mg./kg. spinbath.

The examples that follow illustrate these additional features of the present invention, as well as the use of various other chelate-forming substances.

Example V

A viscose having a cellulose content of 7.7% and an alkali content of 5.5%, to which 0.12% of 5-mercapto-3-p-bromophenyl-2-thio-1,3,4-thiodiazolon-2 and 0.3% of a surface active polyethylene oxide derivative marketed under the name of Hüls V 1011 T had been added, was spun at a xanthate ratio of 0.50, a viscosity of 60 sec. (falling-ball test), and a Hottenroth ripeness of 18.0° in a spinbath at 60° C. containing 6% of H_2SO_4 , 18.5% of Na_2SO_4 and 3.8% of ZnSO_4 . In this bath a tube with

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two portions of different diameter was arranged at a distance of 2 cm. from the spinneret and coaxially therewith, the inlet opening of said tube being flared. The diameter of the tube portion directly in front of the spinneret was 21.5 mm. and the diameter of the second tube portion was 26 mm. The lengths of the narrow and the wide tube portion were 40 and 14 cm., respectively. A cone-shaped tube portion 6 cm. in length constituted the connection between both tube portions. The threads thus spun were finally stretched in a second bath containing 2% of H_2SO_4 and having a temperature of 90° C. The final collecting speed was 80 m./min. The threads thus produced, having a titre of 1840 denier and being composed of 1000 filaments, showed a good skin structure and swelled 70% in water. The dry strength amounted to 4 g./denier at a stretch of 25%. Spinning at the indicated speed was not possible without the use of a tube and a surface-active substance.

Example VI

A viscose with a cellulose content of 8.4% and an alkali content of 4.8% prepared by xanthating with 33% CS_2 , based on cellulose, contained 0.15% 2-mercapto-benzothiazole and 0.04% of a polyethylene oxide derivative available on the market under the name Hüls V 1011 T (both substances calculated on the viscose). The thus-treated viscose was spun with a xanthate ratio of 0.50, a viscosity of 35 sec. (falling-ball test), and a ripeness of 12° Hottenroth, and the spinning bath contained 4.0% H_2SO_4 , 18.0% Na_2SO_4 , 4.0% ZnSO_4 , and the remainder water. The temperature of the spinbath was 50° C. and the immersion stretch was 40 cm. After a stretching of 75% the final draw-off speed amounted to 60 m./min., while in the absence of the polyethylene oxide derivative difficulties occur at draw-off speeds above 40 m./min.

The thread obtained consisted of 200 filaments with a total titre of 400 denier. It had a good skin structure and a swelling capacity of about 70%. The mechanical properties were as follows: dry strength 300 g./100 denier, dry elongation 25%, wet strength 170 g./100 denier, and wet elongation 35%.

It may be noted that various methods have been proposed in the literature from time to time for the manufacture of products from viscose in which products a skin structure is present to a more or less degree. In general such products were obtained by spinning viscose, either with or without specified additives, in zinc-containing spinbaths. In that literature, however, the intermediate formation of zinc chelates in the viscose during the coagulation process has never been disclosed or suggested.

While specific examples of preferred methods and products embodying the present invention have been described above, it will be apparent that many changes and modifications may be made in the methods of procedure and in the products without departing from the spirit of the invention. It will therefore be understood that the examples cited and the methods and procedures set forth above are intended to be illustrative only and are not intended to limit the invention.

What is claimed is:

1. In a process for the manufacture of regenerated cellulose products from viscose by extruding viscose into aqueous H_2SO_4 spinbaths, the improvement that comprises incorporating in the viscose about 0.05–1.0% by weight of the viscose of an organic substance selected from the group consisting of 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolon-2; 5-mercapto-3-p-bromophenyl-2-thio-1,3,4-thiodiazolon-2; and 8-oxyquinoline which is soluble in viscose and which forms with zinc in the product as it is formed, an alkali stable zinc chelate, spinning said viscose in an aqueous sulphuric acid spinbath containing zinc sulphate, and stretching the freshly spun products thereby obtained.

2. A process as defined in claim 1 wherein the organic

substance is 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolon-2.

3. A process as defined in claim 1 wherein the organic substance is 5-mercapto-3-p-bromophenyl-2-thio-1,3,4-thiodiazolon-2.

4. A process as defined in claim 1 wherein the organic substance is 8-oxyquinoline.

5. A viscose spinning solution containing 0.05-1.0% by weight of the viscose of organic substances selected from the group consisting of 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolon-2, 5-mercapto-3-p-bromophenyl-2-thio-1,3,4-thiodiazolon-2 and 8-oxyquinoline.

6. A viscose spinning solution containing 0.05-1.0% by weight of 5-mercapto-3-phenyl-2-thio-1,3,4-thiodiazolon-2.

7. A viscose spinning solution containing 0.05-1.0% by weight of 5-mercapto-3-p-bromophenyl-2-thio-1,3,4-thiodiazolon-2.

8. A viscose spinning solution containing 0.05-1.0% by weight of 8-oxyquinoline.

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