

1

2,942,931

VISCOSE PROCESS

Reid Logan Mitchell, Morristown, N.J., James Wesley Berry, Tucson, Ariz., and William Hughes Wadman, Stockton, Calif., assignors to Rayonier Incorporated, Shelton, Wash., a corporation of Delaware

No Drawing. Filed May 5, 1959, Ser. No. 810,991

6 Claims. (Cl. 18—54)

This invention relates to the viscose process, and has for its object the provision of certain improvements in this process which increase the efficiency of the spinning operation, increase the capacity of the plant, and increase the quality and decrease the cost of the finished yarn or cord. The invention is based on our discovery of the use in the viscose of a mixture of chemicals which we shall refer to as "mixed-modifiers" or as "mixed regeneration retardants" resulting in much higher spinning speeds than is now commercially feasible in the preparation of high-tenacity, "all-skin" filaments, yarns or cords.

We have found that a physical mixture of polyethylene glycol (PEG) and dimethylamine (DMA) is not only a very effective double-action modifier system but, unlike other single modifiers used or proposed as regeneration retardants, the mixed-modifiers of our invention unexpectedly permits increase of the spinning speed to an amazing extent without substantial loss in product quality. The mixed-modifiers have such an effect on the freshly-formed filaments that they can be spun under high tension at greatly increased speed. Each of the retardants PEG and DMA when used alone retards regeneration but does not permit effective high spinning speed. The PEG polymer should have a molecular weight falling in the range of from 400 to 4,000, the preferred range being from 1,000 to 2,000, and the most effective molecular weight being about 1,500. A physical mixture of these two compounds incorporated into the viscose not only permits high stretch (in excess of 100%) imparting superior properties to the filaments but enables filaments having such properties to be spun at greatly increased speed, up to 70 to 90 meters per minute, without undue sacrifice of the desired properties such as high tenacity and long flex fatigue life. Moreover, the mixed-modifiers are highly tolerant and make it possible to use a viscose with a lower salt index (less expensive as it requires less carbon bisulfide), and spin-baths with lower acid and zinc salt contents (the zinc sulfate commonly used is an expensive item in viscose spinning).

When the viscose contains only PEG as retardant, the viscose is fairly easy to spin but the filaments cannot be stretched sufficiently to build high strength, and can be spun effectively only at slow speeds of 20 to 36 meters per minute. When the viscose contains only DMA as retardant, the viscose is readily stretched but has poor spinnability and cannot be spun effectively at a speed higher than about 40 to 50 meters per minute.

No attempt will be made to explain fully the amazing conjoint effect of the mixed-modifiers on permitting use of high spinning speed. Since polyethylene glycols appear to exert a different type of retardant action than amines, the benefit may result from the complementary action by each component of the mixture. Regardless of the accuracy of the explanation, it is clearly apparent that since a physical mixture of the two compounds produces a result which is far greater than the sum of the effects of the compounds used alone that a synergistic

2

action takes place. For example, the use in the viscose of 0.2% of either PEG or DMA alone will permit spinning speeds up to only about 36 to 40 meters per minute in commercial operation in producing good quality yarn, while a mixture of 0.1% each of PEG and DMA will permit spinning speeds in the range of 70 to 90 meters per minute and with no substantial impairment in the physical properties of the filaments.

The synergistic action apparent in spinning with two-class "mixed modifiers," as evidenced by smooth operation, tolerance for high stretch, low acid, low-zinc and retention of high strength, even when spun at speeds approximately double those practical with single-modifiers, appears to stem from the cumulative interaction of the individual retardant effects resulting from the use of polyethylene oxide and the basically different amine.

It is important that the two modifiers be in the form of a simple mixture in the viscose to assure independent action and not a reaction or addition product. It is preferred to add the compounds to the viscose during the mixing stage. Addition may be made separately but it is often convenient to mix the two together in a stock solution prior to addition. Although it is not necessary to use an exact proportion of the two compounds, it is preferred to use about equal proportions by weight of the two compounds for best results, the amount of each compound varying from about 0.05% to 0.5% based on the weight of the viscose. By incorporating the mixed-modifiers into the viscose one can spin filaments and produce the so-called "super-super" cords (1100, 14 x 14) with tenacities in the 5 gram per denier (bone dry range).

The viscose containing the mixed-modifiers may even have formaldehyde added thereto to spin the filaments into a low or zinc-free spin-bath according to the process of our copending patent application Serial No. 811,044, filed May 5, 1959. Since formaldehyde exerts an independent action differing from either polyethylene glycols or amines, such a mixed-modifier system would be termed three-class.

In speculating on the fundamental action of such retardants, one may classify zinc salts with formaldehyde as primary self-sufficient complexing type retardants, and the amines, and polyglycols, as auxiliary, dependent types of retardants requiring the presence of either a zinc salt or formaldehyde to be additionally effective.

The mixed-modifiers effect a control over xanthate regeneration which keeps the filaments in a metastable, stretchable state while they are being stretched, permitting uniaxial orientation of the crystalline elements which are being developed during regeneration. The process effects such a control over the acid penetration rate that the inner portions of the filaments are almost as accessible or responsive as the outer portions to the regenerating reagents thereby permitting a rapid and high degree of stretch and development of structurally "all-skin" filaments.

It is preferred, in forming the viscose, to use cellulose xanthate having a uniform chain length at a degree of polymerization of from 300 to 800, derived from such cellulose as, for example, Rayocord-X, Cordenier-J or other high-alpha cellulose pulps of Rayonier Incorporated, prehydrolyzed kraft, cotton linters, resin-free pulp, cold-caustic refined pulp, high purity pulp of a high degree of polymerization (DP) and uniform chain length, and preoxidized pulp of high purity low DP and uniform chain length.

The process may be carried out with conventional viscose compositions comprising about 7.5% of cellulose and 6.5% of sodium hydroxide, or in any suitable proportions of cellulose to sodium hydroxide varying from

3

4% to 13% of cellulose and from 5% to 13% of sodium hydroxide such as the following:

- 5.0% cellulose and 5.0% caustic soda
- 6.0% cellulose and 5.0% caustic soda
- 7.5% cellulose and 6.5% caustic soda
- 8.0% cellulose and 7.0% caustic soda
- 9.0% cellulose and 8.0% caustic soda
- 10.0% cellulose and 5.0% caustic soda
- 10.0% cellulose and 7.0% caustic soda
- 13.0% cellulose and 13.0% caustic soda

The viscose solution may be prepared according to the usual practice to have a salt (sodium chloride) index varying from 4 to 20, by xanthating the alkali cellulose with the desired amount of carbon bisulfide, say, about 45% of the bisulfide. One may xanthate with the usual 34% of carbon bisulfide and then add to the mixed viscose an additional amount of carbon bisulfide to bring it to the desired sodium chloride index. It is also preferred to spin the viscose into a spin-bath containing from 7 to 10% of sulfuric acid (H_2SO_4), at a temperature of from 50° to 70° C., and to stretch the filaments under controlled conditions in excess of 70%, and preferably above 100% while in contact with the spin-bath. When the usual type of acid-spin bath is used there are advantages in reducing the salt index, say, from 14-20 to 10-12, the H_2SO_4 in the spin-bath from 9-13% to 7-10%, and the $ZnSO_4$ from 6-12% to 1-6%.

EXAMPLES

Example I

A viscose of 7.5% cellulose content and 6.5% sodium hydroxide containing 0.1% polyethylene oxide (Carbowax 1540) and 0.1% dimethylamine added as regeneration retardant was spun at a DP of 450 and sodium chloride salt index of 10.0 into a spin bath containing 7.8 H_2SO_4 , 18.0 Na_2SO_4 and 6.0% $ZnSO_4$ at 60° C. The extruded filaments (1100 in number, to yield a total finished denier of 1650) were led through a 26" tube and for a submerged bath travel of 40", withdrawn from the spin bath and with strong acid bath still clinging thereto, given a multi-stage primary stretch of 115% for a distance of about 60 inches while steaming to keep moist and warm (60° C.). The filaments were then passed through a secondary dilute acid bath containing 4% H_2SO_4 at 90° C. and given an additional stretch of 25% under a tension of 1600 grams, washed, relaxed 2%, treated with 0.1% finishing oil (Stantex 1246), dried, and wound up at a rate of 70 meters per minute.

Filaments of this yarn were "all-skin" and generally round in cross-section. The 1650 denier yarn having 2 t.p.i. gave 5.45 g./denier conditioned tenacity with elongation of 9.5%. When twisted into a 11.5 x 10.5 construction 2 ply cord of 3700 total denier the cord tested 5.0 g./den. bone dry, 4.4 g./den. cond. and 3.4 g./den. wet. Fatigue life index was 1100 (loading of 0.72 g./denier at 150° C.) and 500 (loading of 0.85 g./denier at 150° C.).

When spun alone with 0.2% of added polyethylene oxide, spinning was fair at 50 meters per minute but only 90% total stretch could be given as compared with the 140% above. The resultant cord had 4.0 g./den. conditioned tenacity and a fatigue life of 500 (0.72 g./den. loading). This compares with a viscose control having no added retardant which was spun with 60% stretch, and gave filaments having 2.5 g./denier tenacity and 100 fatigue (0.72 g./den. loading). The spinning was very poor with the retardant free viscose.

When viscose containing 0.2% of dimethylamine was spun, the spinning was only fair at 50 meters per minute but the yarn was quite stretchable and could be given a stretch of 150% total without excessive filament breakage. The resultant cord tested only 4.1 g./den. tenacity and 350 fatigue (0.72 g./den. loading).

4

Good spinning is judged primarily by freedom from broken filaments, roller wraps, worms, encrustations on spinnerets or rollers, etc. Poor spinning is usually apparent in collected fluff at yarn guides, roller wraps, interruptions or breakdown through failure to take normal tension, need for reduced stretch, etc.

Example II

A viscose of 5.0% cellulose and 5.0% sodium hydroxide containing a physical mixture of 0.1% polyethylene glycol (M.W. 1000) and 0.2% dimethylamine as added regeneration retardants was spun at 700 DP and sodium chloride index of 8.0 into a spin bath containing 7.0% H_2SO_4 , 20% Na_2SO_4 , 4.0% $ZnSO_4$ at 70° C. The extruded filaments (1100 in number to yield a total denier of 1100 at windup) were led through a tube, withdrawn from the primary bath but with strong acid still clinging thereto and given a primary multi-stage stretch of 150% for a distance of about 60 inches while heated with steam. The filaments were then passed into a secondary bath containing 3% H_2SO_4 at 95° C. and stretched an additional 50% under a tension of about 1000 grams, washed, relaxed and dried at a windup rate of 90 meters per minute.

Filaments of this yarn were "all-skin" and converted into a 2-ply 14 x 14 twist cord of 2500 denier having a bone dry breaking factor of 28 pounds. The filaments were cut into staple, treated in 1% NaOH at 90° C. to relax them and bleached, SO_2 flushed, washed and dried. The filaments had single filament tenacity of 5.0 gram per denier (conditioned 75° F., 60% RH), wet tenacity of 4.0 g./den. with swelling factor of 70. Such filaments were quite susceptible to resin treatment to reduce elongation and swelling similar to long staple cotton.

Example III

A viscose of 8.0% cellulose and 5.5% sodium hydroxide containing 0.1% polyethylene glycol (M.W. 2000) and 0.1% dimethylamine as added regeneration retardants was spun at 400 DP and sodium chloride index of 6.0 into a spin bath containing 7.0% H_2SO_4 , 20% Na_2SO_4 , 3.0% $ZnSO_4$ at 60° C. The extruded filaments (3000 in number to yield a total denier at windup of 4500) were led through a tube in the primary bath for 30 inches, withdrawn with primary bath clinging thereto, given a multi-stage stretch of 100% over a distance of about 60 inches while heated with steam. They were then passed into a secondary bath containing 4% H_2SO_4 at 95° C. under a tension of 4300 grams and stretched an additional 25%, at a speed of 90 meters per minute. The filaments from this strand were combined with other similar strands into a tow and cut on a bed plate cutter to 1½ inch staple length, washed, desulfured and relaxed in 1% NaOH at 90° C., washed, bleached, again washed, treated with mild SO_2 , and dried.

Single filament tenacity of the staple averaged 4.8 g./den. conditioned at 12% regain and 3.3 g./den. wet. Swelling factor was 73. Such filaments were substantially "all-skin," near-circular in cross-section and had good toughness qualities.

Example IV

A viscose of 7.0% cellulose and 6.0% sodium hydroxide containing 0.2% PEG and 0.2% DMA was spun at 450 DP and salt index of 8.5 into a spin bath containing 7.0% H_2SO_4 , 20% Na_2SO_4 and 4% $ZnSO_4$ at 60° C., withdrawn therefrom without substantial primary stretch, led directly into 4% H_2SO_4 at 90° C. and stretched therein 100% at a speed of 70 meters per minute.

The resulting finished yarn when converted into tire cord had a bone dry tenacity of 5.0 g./den. and fatigue life of 400 (under load of 0.85 g./den.).

It should be recognized that the higher the tenacity level, the more difficult it is to maintain good flexural fatigue life, and, accordingly, the combination of both

5

high strength and fatigue exhibited by the cord produced by the process of the invention indicates a really remarkable advance.

In the course of our extensive investigations, we have evaluated many polyethylene glycols (also called polyethylene oxides) and related polyalkylene compounds, and many amines, in combinations or mixtures, as "mixed-modifiers." We have found that there is a certain amount of synergism resulting from the use in viscose of polymers having appreciable proportions of polyethylene oxide groups, especially when they are terminal groups, mixed with various amines, such as cyclohexylamine, isopropylamine, butylamine and hexamethylamine. However, none of these two-class mixtures, although better than single class modifiers, gives the exceptional increase in spinning speed nor the other aforementioned benefits due to the use of a mixture of PEG and DMA.

This application is a continuation-in-part of our application Serial No. 418,384, filed March 24, 1954.

We claim:

1. The improvement in the viscose process which comprises spinning viscose having therein a regeneration retardant mixture of polyethylene glycol and dimethylamine in the amounts varying from 0.05 to 0.5% each, based on the weight of the viscose, into a coagulating and

6

regenerating acid spin-bath, stretching the filaments at least 70% while in contact with the spin-bath producing high-tenacity filaments capable of being spun in excess of 70 meters per minute.

2. In the process of claim 1 adding the polyethylene glycol and dimethylamine in amounts of about 0.1% each by weight to the viscose prior to spinning.

3. In the process of claim 1 giving a primary stretch to the filaments in excess of 100% and a secondary stretch in excess of 15%.

4. In the process of claim 1 spinning the viscose into a spin-bath containing sulfuric acid in the range of from 5.0% to 13% and zinc sulfate in the range of from 1% to 10%.

5. In the process of claim 1 incorporating formaldehyde into the viscose in addition to the polyethylene glycol and dimethylamine and spinning the viscose into a zinc-free acid spin-bath.

6. In the process of claim 1 using polyethylene glycol having a molecular weight of from 1000-2000.

References Cited in the file of this patent

UNITED STATES PATENTS

2,696,423 Dietrich _____ Dec. 7, 1954