Jan. 23, 1962 R. L. MITCHELL ET AL 3,018,158

VISCOSE PROCESS

Filed May 5, 1959

FIG. 1

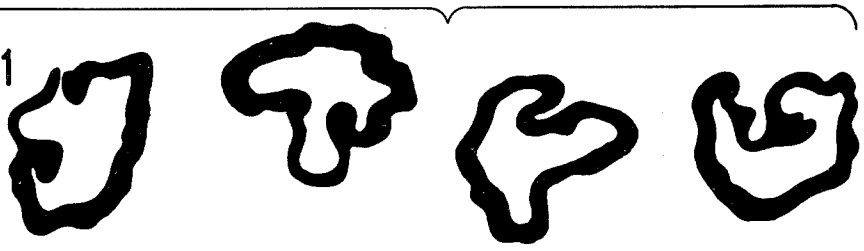


FIG. 2

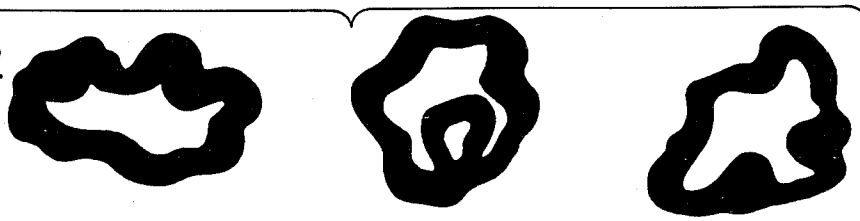


FIG. 3

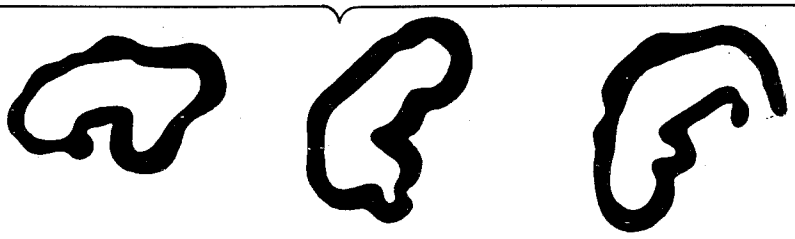


FIG. 4

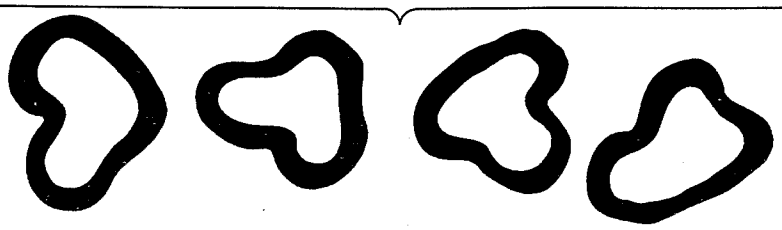


FIG. 5

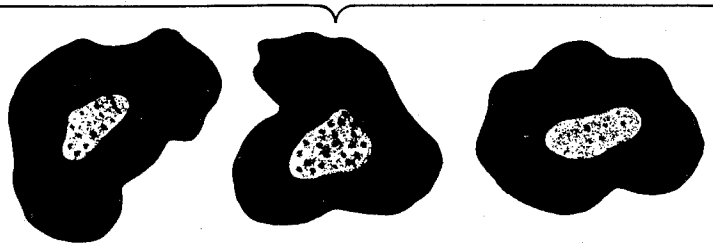
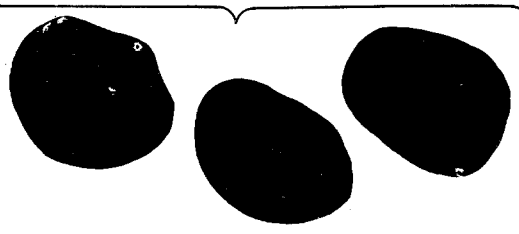


FIG. 6



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United States Patent Office

3,018,158

Patented Jan. 23, 1962

3,018,158

VISCOSE PROCESS

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Filed May 5, 1959, Ser. No. 811,044
5 Claims. (Cl. 18—54)

This invention relates to the viscose process, and has for its object the provision of improvements in this process to effect economies, especially in the spinning operation. The invention is based on the discovery that formaldehyde incorporated into the viscose is a very effective self-sufficient regeneration retardant, permitting the viscose to be spun in a low-zinc or even in a zinc-free acid spin-bath to produce filaments having high tensile strength and other desirable durability, wear and fatigue resistant properties.

The function of zinc salts, such as zinc sulfate, in acid spin-baths to retard regeneration through formation of zinc xanthate complexes enabling the filaments to be stretched during regeneration, is well known. Notwithstanding the high cost of zinc salt, and the fouling of spinnerettes and spin-bath equipment due to its use, there has been no really acceptable substitute for zinc salts as is borne out by the continued universal use of zinc sulfate in the spin-bath. Many other salt substitutes for zinc such as magnesium, aluminum, iron, manganese, etc. have received fleeting attention but none has been really practicable. Many "auxiliary" organic regeneration retardants such as polyethylene oxides, amines, carbamates, etc. for addition to the viscose or in the spin-bath have been proposed and used but, heretofore, none has been found to function in the absence of the zinc salt. An important additional feature is that formaldehyde's effect in the viscose process is independent and additive to the effect of zinc salt, either reducing or eliminating the need for zinc, with corresponding reductions in the cost of production. The invention, accordingly, contemplates the substitution of formaldehyde used in viscose for all, or at least a major portion, of the zinc salt as now used in the acid spin-bath. No other organic modifier, or regeneration retardant now used in conjunction wtih zinc salt will permit such elimination and still produce high-tenacity all-skin filaments.

By incorporating the desired amount of formaldehyde into the viscose solution, the viscose may be spun in an acid spin-bath which is entirely free of zinc salt to produce regenerated filaments, such as the so-called "heavy-skin" and even "all-skin" high tenacity filaments, which are advantageous in the production of tire cord, staple yarns or launderable-type fabrics. It was surprising to find that a small amount of formaldehyde, say, about 0.2% based on the viscose solution, would make it possible to spin the viscose in a zinc-free acid spin-bath at a good rate of speed and to stretch the filaments as much as 80% to 120% to yield an excellent thick-skinned high-tenacity yarn, for example, continuous filament yarns having a conditioned tenacity of 4.6 g./denier, convertible into a cord having a conditioned tenacity of 3.6 g./denier (75° F., 60% RH.).

The formaldehyde prolongs the regeneration period, presumably by formation of a complex with cellulose xanthate, and keeps the filaments in a metastable, stretchable state while they are being stretched, permitting uniaxial orientation of the crystalline elements being developed during regeneration. In the process of the invention the filaments receive a substantially uniform state of decomposition or regeneration throughout their cross-section. The process effects such a control over hydrogen ion (acid) penetration that the inner portions of the filaments are almost as accessible or responsive as the outer portions to the regenerating reagents, the entire cross-

section of the filaments being maintained in an intermediate state of regeneration with high stretchability for a sufficient period to permit a relatively high degree of stretch. Whereas, other known modifiers such as amines and surfactants act only in conjunction with zinc salt to produce the above effects, formaldehyde requires no zinc salt. Other organic modifiers are "auxiliary" retardants facilitating and supplementing zinc salt.

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 pre-oxidized 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 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
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 sodium chloride salt index varying from 4 to 20 and to xanthate 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 45° to 70° C., and to stretch the filaments under controlled conditions in excess of 70% while in contact with the spin-bath.

Preferably, after the viscose has been prepared and during the mixing thereof, the formaldehyde, in amounts varying from, say 0.05 to 1% based on the weight of the viscose, is added to and mixed with the viscose. The viscose solution is spun into a simple coagulating-regenerating spin-bath containing the usual amount of sulfuric acid with or without zinc sulfate. A typical spin-bath without regard to zinc sulfate, or equivalent metal salt, may contain 7.0% sulfuric acid and 20% sodium sulfate. The viscose is extruded through the usual spinnerette into the spin-bath, preferably at a temperature of from 60° C. to 70° C., given primary stretch while in contact with spin-bath carryover of at least 70%, preferably from 70% to 150% and at a temperature of about 60° C., passed into a diluted hot acid bath (4% H_2SO_4) and given a secondary stretch of 20%–50% at a temperature of about 90° C. In an alternative embodiment the filaments may be led without substantial primary stretch into the dilute hot acid and stretched at least 70%.

The resulting filaments may have a thick skin or they may be "all-skin" depending on the variations used during regeneration, the amount of which may be observed by differential dyeing of cross-sections or by phase contrast or by use of an interferometer microscope.

The accompanying drawings are exact copies of typical cross-sections of dyed filaments produced in the viscose process in spin baths free of zinc salt when under

a magnification of 2200×, the dark portions representing the highly oriented or crystalline skin, in which

FIG. 1 illustrates filaments produced as the control and without a zinc salt in the spin bath;

FIG. 2 illustrates filaments produced from viscose containing 0.1% formaldehyde;

FIG. 3 illustrates filaments produced from viscose containing 0.2% of polyethylene glycol;

FIG. 4 illustrates filaments produced from viscose containing 0.2% of dimethylamine;

FIG. 5 illustrates filaments produced from viscose containing 0.4% formaldehyde; and

FIG. 6 illustrates filaments produced from viscose containing 0.4% of formaldehyde, 0.1% dimethylamine, and 0.1% polyethylene glycol.

The following examples illustrate operations carried out according to the process of the invention:

Example I

A viscose of 7.0% cellulose content and 6.0% sodium hydroxide containing 0.4% formaldehyde as a regeneration-retarding xanthate-complexing agent was spun at DP of 500 and sodium chloride salt index of 6.0 into a spin bath containing 7.0% H_2SO_4 and 20% Na_2SO_4 at 70° C. The extruded filaments (1100 in number to yield a yarn of 1650 finished total denier) were led through a 26" tube for a submerged bath travel of 40", withdrawn from the spin bath and with strong acid bath still clinging thereto, given a multistage primary stretch of 85% for a distance of about 60" 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 about 1600 grams, washed, relaxed 2%, treated with 0.1% finishing oil (Stantex emulsion 1246), dried at a rate of 90 meters per minute.

Filaments of this yarn were substantially "skin" as shown in FIG. 5. The 1650 denier yarn having 2 plus t.p.i. gave 5.0 g./denier conditioned tenacity with elongation of 9.0%. When twisted with a 11.5 x 10.5 construction 2-ply cord of about 3700 total denier the cord tested 4.6 g./denier bone dry, 4.0 g./denier conditioned. Fatigue life index was 1100 (loading of 0.72 g./denier at 150° C.).

When spun under similar conditions into the no-zinc bath without formaldehyde in the viscose, only 40% stretch could be applied and the resultant cord had a tenacity of only 2.5 g./denier bone dry, 2.0 g./denier conditioned and a fatigue life index of 100.

When spun into a very low zinc bath same composition as above but with added 1.0% $ZnSO_4$ the action of zinc complemented the formaldehyde and permitted stretching of 120% as compared with 110% without any zinc sulfate. Cord strength was somewhat improved to 5.0 g./denier bone dry, 4.3 g./denier conditions and fatigue life index of 1200.

When spun into the bath containing 1.0% $ZnSO_4$ but no formaldehyde in viscose, stretching of only 60% was possible yielding a cord of 3.0 g./denier bone dry, 2.5 g./denier conditioned and fatigue index of only 120.

Increase of zinc sulfate to 3%, 6% and 9% gave additional improvement but to a decreasing extent. It seems that formaldehyde in viscose is a very effective and economical substitute for all or part of the large amounts of expensive zinc salt in the spin bath.

Combination of formaldehyde in viscose (0.10%), low-zinc sulfate (1%–3%) in the spin bath and "mixed modifiers" in viscose (0.1% each of DMA and Carbowax 1540) as described in a copending application U.S. Serial No. 810,991, now Patent No. 2,942,931, offer a 3-class spinning system for either tire yarn or staple fiber that is far more economical, easier spinning and yields stronger yarn that any other system now known. Spun under conditions similar to above stretching of 150% was possible yielding a cord testing 5.2 g./denier bone dry, 4.5 g./denier conditioned and with a fatigue index of 1200. Such filaments as these cut into relaxed staple fiber yield single filaments with tenacity of 5.2 g./denier conditioned, 4.2 g./denier wet elongation of 18% conditioned. It is further possible to closely approach these same single filament values with 3000 and 7000 hole spinnerettes as well as with the 1100 hole jet used for tire yarn.

Example II

A viscose of 5.0% cellulose content and 5.0% sodium hydroxide containing 0.3% formaldehyde added as a regeneration retardant was spun at DP of 750 and sodium chloride index of 10.0 into a spin bath containing 7.5% H_2SO_4 and 19.5% Na_2SO_4 at 65° C. The extruded filaments (7000 in number to yield a tow of 10,500 total denier) were removed from the spin bath without substantial primary stretch, led directly into 4% H_2SO_4 at 90° C. and stretched therein 100% at a speed of 90 meters/min.

The resulting tow was cut into 1½ inch long staple, washed, finished and dried to yield fiber having single filament strength of 5.0 g./denier bone dry, 4.0 g./denier conditioned, 3.0 g./denier wet.

Example III

The viscose filaments shown in FIGS. 1, 2, 3 and 4 and 6 were produced from a viscose of 7.0% cellulose and 6% sodium hydroxide and were spun into a spin bath and treated under the conditions of Example I with the following exceptions.

The filaments of FIG. 1 contained no regeneration retardant in the viscose and no zinc salt in the spin bath.

The filaments of FIG. 2 were spun from viscose containing 0.1% of formaldehyde and there was no zinc salt in the spin bath.

The filaments of FIGS. 3 and 4 were spun from viscose containing 0.2% each of polyethylene glycol and dimethylamine respectively in spin baths free of zinc salt.

The filaments of FIG. 6 were spun from viscose containing 0.4% formaldehyde, 0.1% dimethylamine, and 0.1% polyethylene glycol in a spin bath free of zinc salt, and stretched about 150%.

This application is a continuation-in-part of our patent application Serial No. 418,384, filed March 24, 1954, and now Patent No. 2,937,922.

We claim:

1. In the viscose process the improvement which comprises forming a viscose spinning solution containing from 4% to 13% of cellulose of relatively uniform chain length at a degree of polymerization level of from 300 to 800 and sodium hydroxide varying from 5% to 13% and having a salt index of from 4 to 20, incorporating in the viscose from 0.05% to 1% based on the viscose of formaldehyde as a regeneration retardant, spinning the viscose into an acid coagulating-regenerating spin-bath containing sulfuric acid in which the retardation of regeneration is effected essentially by the formaldehyde and stretching the resulting filaments during regeneration at least 70% producing high strength thick-skin filaments.

2. In the process of claim 1, spinning the viscose in an acid spin-bath free of zinc sulfate.

3. In the process of claim 1, spinning the viscose in an acid spin-bath containing zinc sulfate which, together with the formaldehyde, give additive effects in the regeneration retardation.

4. In a process for spinning filaments by the viscose process of the type in which a zinc salt has been required in an acid spin-bath as a regeneration retardant, the improvement which comprises including in the viscose a sufficient amount of formaldehyde to serve as regeneration retardant in substitution for from a part to all of the zinc salt.

5. The improved process for spinning high tenacity filaments by the viscose process which comprises including in the viscose at the time of spinning from 0.05% to 1% of

formaldehyde based on the viscose, the amount of formaldehyde being sufficient to serve effectively as a regeneration retardant regardless of whether a zinc salt is contained in the spin-bath, the formaldehyde, together with any zinc salt present, resulting in regeneration retardation of the filaments, and stretching the filaments while in contact with the spin-bath at least 70%.

References Cited in the file of this patent

UNITED STATES PATENTS

2,452,130	Kayser	Oct. 26, 1948
2,479,218	Dosne	Aug. 16, 1949
2,535,044	Cox	Dec. 26, 1950
2,535,045	Cox	Dec. 26, 1950
2,781,275	Baarn	Feb. 12, 1957
2,937,070	Cox	May 17, 1960

OTHER REFERENCES

Hermans, P. H.: "Physics and Chemistry of Cellulose Fibres," Elsevier Publishing Co., Inc., N.Y. (1949), page 367.

Ott, E., et al.: "Cellulose and Cellulose Derivatives," Interstate Publishers, Inc., N.Y. (1946), page 844.