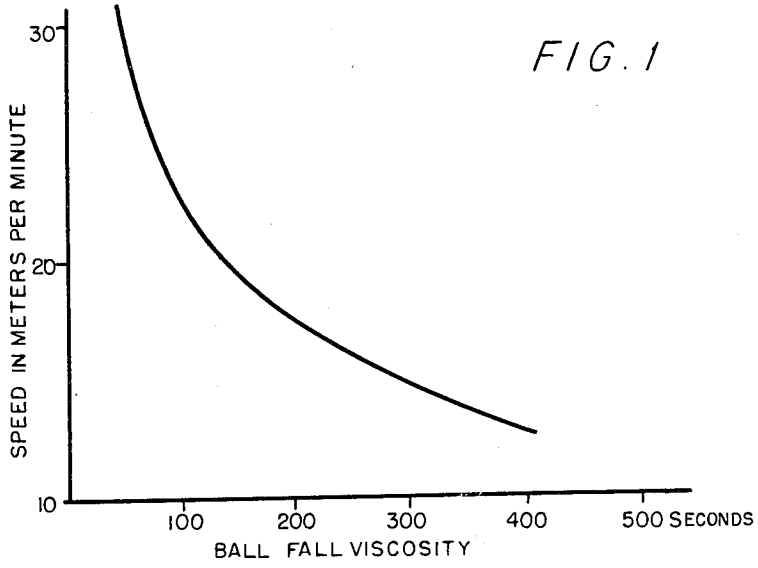
March 24, 1964 E. E. TALLIS ETAL 3,126,435

PRODUCTION OF REGENERATED CELLULOSE FILAMENTS

Filed Dec. 20, 1956

FIG. 1



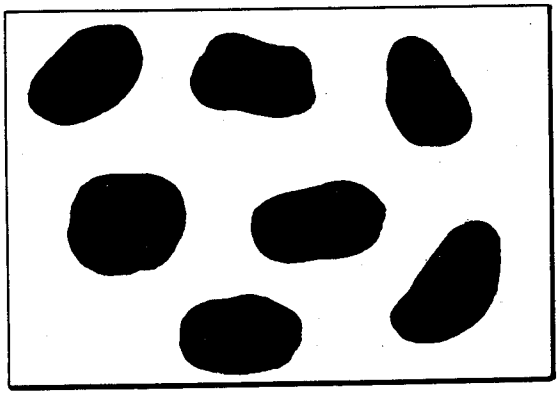


FIG. 2

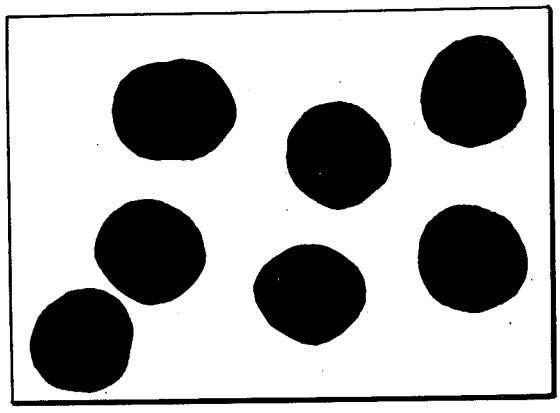


FIG. 3

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United States Patent Office 3,126,435 Patented Mar. 24, 1964

3,126,435

PRODUCTION OF REGENERATED CELLULOSE FILAMENTS

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Filed Dec. 20, 1956, Ser. No. 629,512
Claims priority, application Great Britain Dec. 23, 1955
13 Claims. (Cl. 264—191)

This invention relates to the production of regenerated cellulose filaments and the like from viscose and particularly to the production of such filaments having a high tenacity and which can be twisted into high strength viscose rayon cords.

The tenacity of regenerated cellulose fibres can be increased by subjecting them immediately after spinning to stretching in a hot dilute acid bath, as described in British patent specification No. 467,500. As described in the specification of co-pending patent applications Nos. 581,377 and 582,907, the addition to the viscose of polyethylene oxide or certain polyethylene oxide condensation products enables filaments to be produced having a thick skin and non-crenulated surface with a bean-shaped cross-section and a diffuse boundary between the skin and core. Such filaments have a high wet tenacity and are capable of forming a cord of good tensile properties. The skin and core can be shown, and the skin and core differentiated by a staining technique as described for example in the Textile Research Journal 1945, page 443.

We have now found that a significant improvement in fibre and cord properties particularly in the conditioned state at 65 percent relative humidity can be obtained by spinning, in the presence of polyethylene oxide or polyethylene oxide condensation products, viscose in which the degree of polymerisation of the cellulose is unusually high. We have also found however that the benefit of the longer chain length of the cellulose molecules is only obtained when certain spinning conditions are used, and, in particular, that, for a given value of ball fall viscosity of the viscose there is a critical speed of drawing the threads away from the jet which must not be exceeded if advantage is to be taken of the longer chain length. This critical value is defined by the curve in FIGURE 1 of the accompanying drawings.

The degre of polymerisation (D.P.) was determined from viscosity measurements in 0.5 molar cupriethylene diamine solution. Solutions containing 0.08 to 0.5 percent cellulose were investigated and the specific viscosities (η_{sp}) calculated. The graph of log $\eta_{sp/c}$ against c (the cellulose concentration) was plotted and extrapolated to zero concentration, the intercept enabling the intrinsic viscosity to be calculated according to Martin's equation. In The Staudinger equation relating molecular weight and intrinsic viscosity the constant for this range of degree of polymerisation was taken as 6.4×10^{-3}.

The "ball fall viscosity" is the number of seconds taken for a steel ball of one eighth of an inch diameter to fall through 20 centimetres of viscose at 15° C.

According to the invention therefore, regenerated cellulose filaments having a substantially circular or bean-shaped cross-section and a substantially all-skin structure are produced by extruding viscose, the cellulose of which has an average degree of polymerisation of at least

400, at a salt point between 6 and 15, preferably from 8.5 to 12, into an aqueous coagulating bath containing sulphuric acid together with zinc sulphate and sodium sulphate, the total salt content preferably not exceeding 24 percent by weight, in the presence of between 0.5 and 10 percent by weight of the weight of the cellulose of a polyethylene oxide of average molecular weight between 300 and 10,000, preferably between 600 and 6,000, at a draw-off speed not substantially greater than that defined by the curve shown in FIGURE 1.

To develop high tenacity, the filaments should be subjected to hot-stretching, in accordance with British patent specification No. 467,500, in a hot aqueous acid bath preferably containing at least 3 percent of sulphuric acid. Regeneration of the filaments should be substantially complete when the filaments leave this bath.

The salt point is defined in its normal sense, as the percentage strength of an aqueous sodium chloride solution required just to coagulate the viscose at 15° C.

Where practicable, improved properties are obtained by spinning at an extrusion ratio less than one. The extrusion ratio is the ratio of the speed at which the filaments are drawn from the jet to the speed at which the viscose passes through the jet orifices.

The polyethylene oxide is preferably added to the viscose and may be added in the form of a condensation product as described in the specification of application No. 13306/55.

For any given content of caustic soda in the viscose and spinning speed, the sum of the cellulose content of the viscose and the best concentration of spinning bath acid, both expressed as a percentage, is approximately constant. For example, for a concentration of 7 percent caustic soda and a draw-off speed of 14 metres per minute, the constant is equal to from 12 to 13.

Preferably, the zinc sulphate concentration in the bath is 6 to 15 percent. The best yarn results have so far been obtained with 6 to 7 percent cellulose, 7 percent soda, 6 to 7 percent acid, 10 percent zinc sulphate, 3 percent polyethylene oxide on the weight of cellulose and an extrusion ratio of 0.7.

When the viscose has a cellulose content of 5 percent or less, the ball fall viscosity should be preferably from 25 to 67, and the percentage of sulphuric acid in the coagulating bath should be from 0.9 to 1.5 (preferably 1.15 to 1.40) times the percentage of caustic soda in the viscose. The coagulating bath should contain 3 to 15 percent zinc sulphate.

Example 1

Viscose containing 6.0 percent cellulose of average DP 585, 7.0 percent soda and 3 percent on the cellulose of a polyethylene oxide condensate of average molecular weight 1,000, and with a spinning ball fall viscosity of 100 seconds is spun at an extrusion ratio of 0.7 and at a salt figure of 9.2 into a spin bath flowing through a tube concurrently with the filaments, and containing 7.0 percent sulphuric acid, 12.0 percent zinc sulphate and 11.0 percent sodium sulphate at 55° C. The draw-off speed was 14 metres per minute. The yarn was stretched 95 percent through a second bath at 95° C. containing 3.0 percent sulphuric acid and less than 1.5 percent total

salts and after washing, drying on a heated drum and collecting had the following properties:

Denier	1640, 1,000 filaments.
Oven dry tenacity	5.76 grams per denier.
Oven dry extensibility	9.3 percent.
Conditioned tenacity (65 percent relative humidity)	5.01 grams per denier.
Conditioned extensibility	13.7 percent.
Wet tenacity	3.79 grams per denier.
Wet extensibility	24.2 percent.

The filaments were twisted into a yarn with 12 S twist and two such yarns were twisted together into a 12 Z cord. The cord properties were:

Denier	3800.
Oven dry breaking load	35.80 lbs.
Oven dry tenacity	4.25 grams per denier.
Oven dry extensibility	15.3 percent.
Conditioned breaking load (65 percent relative humidity)	29.6 lbs.
Conditioned tenacity	3.54 grams per denier.
Conditioned extensibility	24.0 percent.

Typical cross-sections of the filaments are shown in FIGURE 2 of the accompanying drawings. The sections are nearly round and only slightly bean shaped, and are of uniform structure, consisting throughout of skin.

Example 2

Viscose containing 7.0 percent cellulose of average DP 585, 7.0 percent caustic soda and 4 percent on the cellulose of a polyethylene oxide condensate of average molecular weight 1,000, and having a spinning ball fall viscosity of 220 was spun at an extrusion ratio of 0.7 and at a salt figure of 10.4 into a spin bath containing 6.0 percent sulphuric acid flowing through a tube with the filaments, 7.0 percent zinc sulphate and 11.0 percent sodium sulphate at 55° C. The first reel speed was 14 metres per minute. The yarn was stretched 95 percent through a second bath containing 3.0 percent sulphuric acid and less than 1.5 percent total salts at 95° C., and after washing, drying on a heated drum and collecting had the following properties:

Denier	1666, 1,200 filaments.
Oven dry tenacity	5.88 grams per denier.
Oven dry extensibility	8.9 percent.
Conditioned tenacity	5.50 grams per denier.
Conditioned extensibility	13.4 percent.
Wet tenacity	3.84 grams per denier.
Wet extensibility	26.2 percent.
12 S x 12 Z cord denier	3,900.
Oven dry breaking load	36.95 lbs.
Oven dry tenacity	4.30 grams per denier.
Oven dry extensibility	12.9 percent.
Conditioned breaking load	30.6 lbs.
Conditioned tenacity	3.57 grams per denier.
Conditioned extensibility	22.3 percent.

Typical cross-sections are shown in FIGURE 3 of the accompanying drawings.

Example 3

As Example 2 with the following conditions:

Viscose:
- 6.5 percent cellulose of average DP 585.
- 7.0 percent soda.
- 4 percent polyethylene oxide.
- Spinning ball fall viscosity 160.
- Salt figure 8.6.
- Extrusion ratio 0.7.

Bath:
- 6.5 percent sulphuric acid.
- 10.0 percent zinc sulphate.
- 11.0 percent sodium sulphate.
- 55° C.

Draw-off speed:
- 14 metres per minute.
- 95 percent stretch.

The yarn properties were as follows:

Denier	1630, 1,200 filaments.
Oven dry tenacity	6.38 grams per denier.
Oven dry extensibility	8.9 percent.
Conditioned tenacity	5.68 grams per denier.
Conditioned extensibility	11.7 percent.
Wet tenacity	4.30 grams per denier.
Wet extensibility	27.3 percent.

Example 4

As Example 2 with the following conditions:

Viscose:
- 6.0 percent cellulose of average DP 585.
- 7.0 percent soda.
- 2 percent polyethylene oxide.
- Spinning ball fall viscosity 115.
- Extrusion ratio 0.7.
- Salt figure 10.6.

Bath:
- 6.5 percent sulphuric acid.
- 7.0 percent zinc sulphate.
- 11.0 percent sodium sulphate.
- 55° C.

Draw-off speed:
- 22 metres per minute.
- 85 percent stretch.

The yarn and cord properties were as follows:

Denier	1696, 1,200 filaments.
Oven dry tenacity	5.72 grams per denier.
Oven dry extensibility	8.0 percent.
Conditioned tenacity	5.13 grams per denier.
Conditioned extensibility	12.6 percent.
Wet tenacity	4.01 grams per denier.
Wet extensibility	27.0 percent.
12 S x 12 Z cord denier	3970.
Oven dry breaking load	35.75 lbs.
Oven dry tenacity	4.09 grams per denier.
Oven dry extensibility	14.7 percent.
Conditioned breaking load	30.2 lbs.
Conditioned tenacity	3.46 grams per denier.
Conditioned extensibility	23.6 percent.

In general it appears that cross-sections become more circular as viscosity increases, and that yarn properties improve provided the critical draw-off speed is not exceeded.

Example 5

This example shows the effect of too high a spinning speed for a particular viscosity or vice versa.

The procedure was as in Example 2 with the following conditions:

Viscose:
- 7.0 percent cellulose of average DP 585.
- 7.0 percent soda.
- 3 percent on the polyethylene oxide.
- Spinning ball viscosity 210.
- Salt figure 10.8.
- Extrusion ratio 0.7.

Bath:
- 8.0 percent sulphuric acid.
- 12.0 percent zinc sulphate.
- 11.0 percent sodium sulphate.
- 55° C.

Draw-off speed:
- 22 metres per minute.
- 85 percent stretch.

The yarn and cord properties were as follows:

Denier	1592, 1,000 filaments.
Oven dry tenacity	4.84 grams per denier.
Oven dry extensibility	7.8 percent.
Conditioned tenacity	3.77 grams per denier.
Conditioned extensibility	10.5 percent.
Wet tenacity	2.65 grams per denier.
Wet extensibility	19.0 percent.
12 S x 12 Z cord denier	3715.
Oven dry breaking load	24.25 lbs.
Oven dry tenacity	2.96 grams per denier.
Oven dry extensibility	11.2 percent.
Conditioned breaking load	21.5 lbs.
Conditioned tenacity	2.64 grams per denier.
Conditioned extensibility	19.1 percent.

In all the foregoing examples the yarns were stretched 95 percent in a second bath containing 3.0 percent sulphuric acid and less than 1.5 percent total salts, at 95° C., as in Examples 1 and 2.

Example 6

Viscose containing 5.0 percent of cellulose of average DP 585, 7.0 percent of caustic soda and 42 percent of carbon disulphide based on the weight of the α cellulose, containing 2.0 percent by weight based on the weight of the cellulose of a polyethylene oxide of average molecular weight 1000 and having a viscosity of 54 poises (Ball Fall 45) was extruded at a salt figure of 10.5 through a jet having 750 holes each 0.0025 inch in diameter at an extrusion ratio of 0.45 into an aqueous coagulating bath containing 8.8 percent of sulphuric acid, 12.0 percent of sodium sulphate and 10.0 percent of zinc sulphate at 60° C. at a draw-off speed of about 22 metres per minute. The length of immersion of the filaments in the bath was 30 inches and the 750 filament yarn formed was withdrawn from the bath by a reel and was passed through a hot aqueous acid bath at 95° C. to a second reel rotating at a speed faster than that of the first reel to impart a stretch of 87 percent to the filaments. The hot aqueous acid bath contained 3.0 percent of sulphuric acid, 0.8 percent of sodium sulphate and 0.4 percent of zinc sulphate. The stretched yarn had a speed of 40 metres per minute. The yarn was subsequently treated with a dilute acid bath of the same constitution as the hot aqueous acid bath in which the yarn was stretched without relaxation until regeneration was substantially complete and then washed with water, treated with a finish, dried and collected.

The yarn had a denier of 1640 and the following physical properties:

Bone dry tenacity	5.37 grams per denier.
Bone dry extensibility	8.8 percent.
Tenacity after conditioning at relative humidity of 65 percent	4.70 grams per denier.
Extensibility after conditioning at relative humidity of 65 percent	11.2 percent.
Wet tenacity	3.38 grams per denier.
Wet extensibility	24.3 percent.
Bone dry cord breaking load	33.10 lbs.
Bone dry cord tenacity	3.92 grams per denier.
Bone dry cord extensibility	14.4 percent.
Cord breaking load after conditioning at relative humidity of 65 percent	28.8 lbs.
Cord tenacity after conditioning at relative humidity of 65 percent	3.41 grams per denier.
Cord extensibility after conditioning at relative humidity of 65 percent	20.3 percent.

The cord was made by twisting yarns having an S twist of 12 turns per inch and then doubling two of the twisted yarns with a Z twist of 12 turns per inch. The cord obtained had a denier of 3840.

Example 7

Viscose containing 5.0 percent of cellulose of average DP 580, 8.0 percent of caustic soda and 42 percent of carbon disulphide based on the weight of the α-cellulose, containing 2.0 percent by weight based on the weight of the cellulose of a polyethylene oxide of average molecular weight 1000 and having a viscosity of 38 poises (Ball Fall 32) was extruded at a salt figure of 9.8 through a jet having 750 holes each 0.0025 inch in diameter at an extrusion ratio of 0.4 into an aqueous coagulating bath containing 10.6 percent of sulphuric acid, 12.0 percent of sodium sulphate and 10.0 percent of zinc sulphate at 60° C. at a draw-off speed of 21 meters per minute. The remaining conditions of spinning and treatment were as in Example 1.

The yarn had a denier of 1634 and the following physical properties:

Bone dry tenacity	5.37 grams per denier.
Bone dry extensibility	8.6 percent.
Tenacity after conditioning at relative humidity of 65 percent	4.87 grams per denier.
Extensibility after conditioning at relative humidity of 65 percent	12.7 percent.
Wet tenacity	3.03 grams per denier.
Wet extensibility	23.3 percent.
Bone dry cord breaking load	33.50 lbs.
Bone dry cord tenacity	3.98 grams per denier.
Bone dry cord extensibility	14.4 percent.
Cord breaking load after conditioning at relative humidity of 65 percent	28.35 lbs.
Cord tenacity after conditioning at relative humidity of 65 percent	3.36 grams per denier.
Cord extensibility after conditioning at relative humidity of 65 percent	20.2 percent.

The cord was made by twisting yarns having an S twist of 12 turns per inch and then doubling two of the twisted yarns with a Z twist of 12 turns per inch. The cord obtained had a denier of 3820.

Example 8

Viscose containing 4.96 percent of cellulose of average DP 580, 6.99 percent of caustic soda and a total sulphur content of 1.76 percent, containing 2.0 percent by weight based on the weight of α-cellulose of a polyethylene oxide of average molecular weight 1500 and having a ball fall viscosity of 45, was extruded at a salt figure of 10.7 through a jet having 10,000 holes each 0.003 inch in diameter at an extrusion ratio of 1.1 into an aqueous coagulating bath containing 7.1 percent of sulphuric acid, 9.35 percent of zinc sulphate and 16.4 percent of sodium sulphate at 55° C. at a draw-off speed of 9 metres per minute. The length of immersion of the filaments in the coagulating bath was 10½ inches and the 10,000 filament yarn formed was withdrawn from the bath by a reel and was passed through a hot aqueous acid bath at 93° C. to a second reel rotating at a speed faster than that of the first reel to impart a stretch of 84 percent to the filaments. The hot aqueous acid bath contained 2.1 percent of sulphuric acid and 1.30 percent of sodium sulphate. The final denier of the yarn was 15,000, having a denier per filament of 1.5. The cross-sections of the filaments when spun exhibited an all skin structure and were bean-shaped. The wet tenacity of the single filaments was 4.25 grams per denier. The wet extensibility was 31.0 percent.

Filaments spun under similar conditions but with viscose containing 7.5 percent of cellulose of a DP of about 350

exhibited a wet tenacity of about 3.4 grams per denier and the same extensibility.

What we claim is:

1. A process for producing regenerated cellulose filaments having a substantially all skin structure, comprising extruding viscose having a ball fall viscosity of between about 44 and about 410 seconds, the cellulose of which has an average degree of polymerisation of at least 400 at a salt point between 6 and 15, into an aqueous coagulating bath containing sulphuric acid together with zinc sulphate and sodium sulphate in the presence of between 0.5 and 10 percent by weight of the weight of the cellulose of a polyethylene oxide of average molecular weight between 300 and 10,000 at an extrusion ratio of between about 0.4 and about 1.1 and at a draw-off speed not substantially greater than the draw-off speed determined by applying the ball fall viscosity of the viscose to the curve shown in FIGURE 1.

2. A process according to claim 1 in which the filaments have a substantially circular cross-section.

3. A process according to claim 1 in which the filaments have a substantially bean-shaped cross-section.

4. A process according to claim 1, in which upon emerging from the coagulating bath, the filaments are stretched in a hot acid bath.

5. A process according to claim 1, in which the salt point of the viscose is between 8.5 and 12 inclusive.

6. A process according to claim 1, in which the total salt content of the coagulating bath does not exceed 24 percent by weight.

7. A process according to claim 1, in which the viscose is extruded at an extrusion ratio of less than 1.

8. A process according to claim 1, in which the average molecular weight of the polyethylene oxide is between 600 and 6,000.

9. A process according to claim 1, in which the polyethylene oxide is added to the viscose.

10. A process according to claim 1, in which the concentration of zinc sulphate in the coagulating bath is from 6 to 15 percent by weight.

11. A process according to claim 4, in which the viscose contains from 6 to 7 percent cellulose, 7 percent caustic soda and 3 percent of polyethylene oxide based on the weight of cellulose, the coagulating bath contains 6 to 7 percent acid, 10 percent zinc sulphate and in which the viscose is extruded at an extrusion ratio of 0.7.

12. A process according to claim 1, in which the viscose contains not more than 5 percent of cellulose and has a ball fall viscosity of from 44 to 67 seconds, the percentage of sulphuric acid in the coagulating bath is from 0.9 to 1.5 times the percentage of caustic soda in the viscose, and the bath contains 3 to 15 percent of zinc sulphate.

13. A process according to claim 12, in which the percentage of sulphuric acid in the coagulating bath is from 1.15 to 1.40 times the percentage of caustic soda in the viscose.

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