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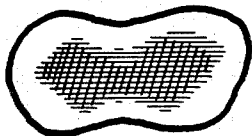
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SPINNING OF VISCOSE  
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*Fig. 1.*



*Fig. 2.*



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## UNITED STATES PATENT OFFICE

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## SPINNING OF VISCOSE

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**1** This invention relates to the regeneration of cellulose from viscose. More particularly, it relates to a new process for manufacturing regenerated cellulose articles such as filaments or films having improved properties.

Although the invention is generally applicable to the preparation of filaments, yarns, films, caps, bands, ribbons, and other structures or regenerated cellulose, it will be discussed with particular reference to the production of viscose rayon yarn.

It is known that the general strength and quality of viscose yarns are improved through reduction of the primary swelling of the gel fibers. The great importance of the gel swelling factor in viscose spinning operations has attained full recognition only in the last few years (see, for example, U. S. 2,347,883 and 2,347,884). It is now recognized that, to constitute a commercially useful viscose rayon process, the viscose composition and the composition of the sulfuric acid coagulating bath must be so balanced as to permit the production of regenerated cellulose filaments having a gel swelling factor of not more than about 6.5. It has been found that, for a given viscose, yarn properties such as tenacity, elongation, softness, etc., are, as a rule, best when spinning is done at or near the point of minimum gel swelling. It has been found, moreover, that yarn properties are improved through methods designed to reduce the gel swelling factor below the above-mentioned value of 6.5 and that, in general, the greater the reduction, the more marked the improvements. Already proposed methods of reducing the gel swelling factor include the addition to the coagulating bath of zinc sulfate or of ferrous, manganous, or chromic sulfates (U. S. Patents 2,364,273; 2,347,883; and 2,347,884). While these methods represent valuable advances in the art, further improvements in yarn properties are needed.

It is well known that unripened viscoses (the so-called "green" viscoses), i. e., viscoses of salt index of about 7 or higher, are not suitable for spinning by the methods currently used in the industry with normally ripened viscoses, i. e., viscoses of salt index of about 5 to 6 or lower. This is attributed to the high primary gel swelling of green viscoses, even though their high degree of xanthation (which is reflected in propor-

**2** tionately high salt index values) has been thought desirable on theoretical grounds for viscose spinning. A further problem, then, is to make unripened viscose of high salt index amenable to spinning. This is highly desirable since the use of unripened viscose would result in decreasing or eliminating the ripening time now necessary in manufacturing practice. Accordingly, methods for further reducing the gel swelling factor of unripened viscose, and in particular, methods involving further improvements in yarn properties are particularly desirable.

An object of this invention is to provide a process of manufacturing regenerated cellulose filaments having gel swelling values lower than heretofore attainable and exhibiting considerably improved yarn properties. Another object is to provide a process whereby unripened viscose can be spun in conventional spinning equipment to give yarn of high quality. A further object is to provide a process of manufacturing regenerated cellulose yarn having entirely novel and desirable properties. Yet a further object is the provision of a high tenacity, high fatigue resistant regenerated cellulose fiber having a non-crenulated surface and having improved soil and abrasion resistance. Other objects will appear hereinafter.

These objects are accomplished, in accordance with the invention, by extruding viscose into a sulfuric acid-sodium sulfate coagulating bath containing zinc sulfate and stretching the filament, preferably in a secondary bath, the coagulation of the gel filament being carried out so that it is in contact with small amounts of a water-soluble organic quaternary ammonium compound, i. e., hydroxide or salt, in which each of the four organic radicals attached to the nitrogen contains not more than four aliphatic carbons, at least three of these organic groups being completely aliphatic and the fourth one, when aromatic, containing only one benzene nucleus, said quaternary ammonium compound having no appreciable surface tension lowering properties.

Another object, which it was unexpectedly found possible to accomplish through the invention described below, was the production of very high strength yarns having smooth (non-crenulated) surfaces. These yarns have substantially

improved soil resistance and abrasion resistance. The combination of high tenacity and high fatigue resistance with smooth surface had not heretofore been achieved.

The use of certain quaternary ammonium compounds in viscose coagulating baths for the purpose of preventing or reducing incrustation of the spinnerets is well known (see, for example, U. S. Patent 2,125,031). As the prior investigators have very clearly pointed out, the materials which can be used for that purpose must be surface-active. This means, in terms of chemical constitution, that such quaternary ammonium compounds must have at least one long chain alkyl group of at least 6, and preferably at least 12 carbon atoms. The prior art did not contemplate, and, in fact, positively excluded, the use of non-surface-active, short-chain quaternary ammonium compounds, which are, indeed, ineffective for the purpose of preventing spinneret incrustation. There was, therefore, no reason to expect that the non-surface-active, short-chain compounds would have any effect whatever on viscose spinning and/or yarn properties, and even less reason to expect that their use would decrease the gel swelling factor of the yarn below any previously known minimum and permit the production, from either ripened or unripened viscose, of high tenacity filaments possessing certain entirely new properties. That these advantages are, in fact, obtained through the use of non-surface-active, short-chain quaternary ammonium compounds is particularly remarkable since the similar, but long-chain, surface-active compounds of the art are incapable of producing these results. This indicates that the quaternary compounds used in this invention are highly selective viscose or bath modifying agents and that their use provides solutions to the several problems outlined above in a surprising manner.

By the term "water-soluble, non-surface-active quaternary ammonium compounds" is meant those quaternary ammonium compounds which, in concentrations of 0.1%, do not lower the surface tension of distilled water at 25° C. by more than about 6 dynes per centimeter. Such quaternary ammonium compounds may contain four aliphatic groups attached to the nitrogen atom none of which groups are more than 4 carbon atoms in length or they may contain three of such groups, the fourth group being then aromatic and containing only one phenyl group. The anions in every instance are devoid of surface activity.

Referring to the drawings:

Figure 1 is a dyed cross section of a filament regenerated from an unripened, unmodified viscose, and

Figure 2 is a dyed cross section of a filament regenerated from an unripened, modified viscose of this invention.

The invention will be more clearly understood by referring to the examples and discussion which follow. The numerical values of gel swelling given below for various yarn samples were all determined according to the following procedure. The gel thread was collected in a monolayer on a bobbin, by manually operating a traverse mechanism with the thread being stretched 80% in the hot dip bath. The sample was centrifuged (1400 R. P. M.) for one minute, cut off, and weighed in a closed bottle. The sample was washed free of acid, dried in an oven at 105° C.,

and weighed. The ratio of the gel weight to cellulose weight (grams of gel per gram of cellulose) is referred to as the gel swelling. Variations may be introduced in the procedure, e. g., in the stretch, spinning speed, or length of bath travel, but these introduce only minor changes in the numerical values of gel swelling.

Another important indication of yarn quality is the factor referred to below as "D" value. This factor relates to the rate of neutralization of the viscose filament in the coagulating and regenerating bath. It is determined by adding to the viscose a suitable indicator, in this case bromocresol purple (pH range 5.2 to 6.8), and observing the distance in inches from the spinneret at which point the purple color completely disappears in the traveling filament. This distance is the "D" value. The selected quaternary ammonium compounds suitable for use in this invention reduce the rate of neutralization of the spinning filaments, hence increase the "D" value over that of unmodified viscose. It has been found that, in general, the greater the "D" value or the slower the rate of neutralization, the better the yarn properties. It is believed that the increased "D" value is an indication that the modifying agents of this invention permit greater dehydration of the viscose before the gel structure of the filament is permanently set.

In the following examples parts and percentages are by weight. These examples are given for illustrative purposes and are not to be construed in any sense as limitative.

#### EXAMPLE I

Four viscoses containing 0, 0.78, 1.6 and 9.0 millimoles of benzyltrimethylammonium hydroxide per 100 grams of viscose are prepared in the following manner using 7% cellulose and 6% total sodium hydroxide (7 to 6 viscose). Alkali cellulose aged to get the desired viscose viscosity (40 to 60 poises) is xanthated for 2½ hours using 35% CS<sub>2</sub> (based on the recoverable bone-dry cellulose). Xanthated crumbs are dissolved in a solution of caustic containing the modifier in the amounts mentioned above. After mixing 1½ hours at 0° C., the freshly prepared viscoses is filtered while it is cold, deaerated, and kept at 0° C. until spun. It is spun in the unripened state, as shown by the high salt index values, high xanthate sulfur content, and low sodium trithiocarbonate content. In all examples, the caustic content of 6% refers to the total alkalinity expressed as sodium hydroxide. It includes the benzyltrimethylammonium hydroxide and the free sodium hydroxide and that combined in the form of sodium carbonate, sodium trithiocarbonate, and sodium cellulose xanthate.

The viscose is spun into 275 denier-100 filament yarn by extruding through a spinneret having holes of 0.0025-inch diameter into primary coagulating and regenerating baths comprising (1) 6.0% H<sub>2</sub>SO<sub>4</sub>, 14% Na<sub>2</sub>SO<sub>4</sub>, and 15% ZnSO<sub>4</sub>, and (2) 9% H<sub>2</sub>SO<sub>4</sub>, 22% Na<sub>2</sub>SO<sub>4</sub>, 1% ZnSO<sub>4</sub>, and 5% FeSO<sub>4</sub>. The yarn is given a bath travel of 28 inches by using a roller guide. The apparatus and general procedure used to lead viscose into the bath and to collect the formed thread are essentially the same as those used commercially in the so-called bobbin or spool process. The specific conditions include a bath temperature of 50° C. and a first feed wheel speed of 485 inches

per minute. The filaments are carried through a water bath at 95 to 100° C. and wound up at such a speed as to give 80% stretch beyond the feed wheel. The resulting regenerated gel yarn is washed free of acid and salt and then processed. The yarns which are dried on the bobbin or, alternately, partially relaxed before drying by rewinding on another bobbin, are twisted 4 turns per inch and tested after conditioning at 21° C. and 60% relative humidity for 48 hours.

The properties of the yarn prepared from the viscoses described herein are listed in Table IA together, for comparison, with those of unripened, unmodified viscose and of ripened, un-

per 100 grams of viscose. Both yarns of Figures 1 and 2 were prepared using a coagulating bath designated as

9.5-14-15 ( $H_2SO_4-Na_2SO_4-ZnSO_4$ )

The skin of regular viscose yarn may be shown very graphically by a special dye technique. When the cross sections are soaked in 0.2% Pontamine Sky Blue dye for 10 to 60 minutes, the core takes on a deep blue color while the skin remains undyed. However, with yarns from viscoses modified with quaternary ammonium salts, the dye boundary is diffused and no great contrast in shades between the skin and core is visible, as is shown in Figure 2.

Table IA

| Example  | Salt Index | Per Cent Xanthate Sulfur | Na <sub>2</sub> CS <sub>4</sub> Per Cent | Modifier Milli-moles/100 g. Viscose | Tenacity g./d. |      |      | Elongation, Per Cent |      |      | Gel Swelling | "D" Value in. |
|--|------------|--------------------------|--|-------------------------------------|----------------|------|------|----------------------|------|------|--------------|---------------|
|  |            |                          |  |                                     | Dry            | Wet  | Loop | Dry                  | Wet  | Loop |              |               |
| COAGULATING BATH 8-14-15 ( $H_2SO_4-Na_2SO_4-ZnSO_4$ )           |            |                          |  |                                     |                |      |      |                      |      |      |              |               |
| 1-----   | 8+         | 1.40                     | 0.63                                     | 0                                   | 3.60           | 1.90 | 2.74 | 8.5                  | 18.5 | 6.7  | 3.11         | 1.8           |
| 2-----   | 8+         | 1.40                     | 0.70                                     | 0.78                                | 3.90           | 2.47 | 3.16 | 9.4                  | 23.0 | 6.5  | 2.73         | 3.5           |
| 3-----   | 8.1        | 1.40                     | 0.60                                     | 1.50                                | 3.88           | 2.72 | 2.97 | 7.8                  | 20.2 | 5.3  | 2.61         | 6.0           |
| 4-----   | 8.6        | 1.35                     | 0.72                                     | 9.0                                 | 4.0            | 2.78 | 2.72 | 8.8                  | 19.0 | 5.1  | 2.59         | 7.0           |
| 5-----   | 5.0        | 1.15                     | 1.30                                     | 0                                   | 3.68           | 2.22 | 2.10 | 8.9                  | 20.5 | 4.5  | 3.18         | 2.5           |
| COAGULATING BATH 8.5-22-1-5 ( $H_2SO_4-Na_2SO_4-ZnSO_4-FeSO_4$ ) |            |                          |  |                                     |                |      |      |                      |      |      |              |               |
| 6-----   | 8+         | 1.40                     | 0.63                                     | 0                                   | 3.44           | 1.76 | 2.26 | 9.5                  | 16.0 | 7.4  | 3.53         | 2.2           |
| 7-----   | 8+         | 1.40                     | 0.60                                     | 0.78                                | 3.70           | 2.43 | 2.50 | 7.9                  | 19.8 | 4.6  | 2.64         | 5.0           |
| 8-----   | 8.1        | 1.40                     | 0.70                                     | 1.50                                | 3.60           | 2.40 | 2.20 | 7.0                  | 18.4 | 3.6  | 2.65         | 6.0           |
| 9-----   | 8.6        | 1.35                     | 0.72                                     | 9.0                                 | 3.94           | 2.55 | 2.30 | 8.0                  | 15.2 | 4.1  | 2.66         | 7.0           |
| 10-----  | 5.0        | 1.15                     | 1.30                                     | 0                                   | 3.70           | 2.29 | 2.0  | 7.7                  | 18.1 | 3.4  | 3.52         | 2.2           |

modified viscose (the standard viscose of commercial operation), both controls being spun under conditions identical to those for the modified viscoses. It will be seen that the level of properties is lowest for the yarns from the unripened, unmodified viscoses. In all cases, the wet strengths of yarns from the unripened, modified viscoses of this invention are greater than those for ripened, control viscoses.

The yarn produced by this and the other examples has a number of remarkable properties which distinguish it sharply from other regenerated cellulose yarns. The most readily apparent of these new features are the cross-section and the surface. The cross sections of viscose yarn are observed and studied in the following manner. After imbedding the yarn in paraffin, cross sections are cut and affixed to a glass slide by a shellac cement. After removing the paraffin in xylene, the sections are swollen in water and photomicrographs are taken. For yarns prepared from unripened, unmodified viscose spun into zinc baths, a skin or outer shell which swells to a different extent from that of the core is visible. These yarn cross sections show both deep and shallow crenulations around the contour of the filament, as shown in Figure 1. However, for yarns of this invention, as, for example, those spun into zinc baths from viscose modified with non-surface-active quaternary ammonium compounds, the boundary between the skin and core is very diffuse and crenulations are absent, giving the yarn a smooth surface, as indicated in Figure 2. The yarn of Figure 2 is unripened viscose obtained using 9 millimoles of benzyltrimethylammonium hydroxide

40 The filaments of this invention having smooth surfaces, i. e., showing no appreciable crenulation, have outstanding resistance to soiling, fibrillating, and laundering. Fatigue resistance is also materially improved.

45 The yarn from viscose spun in contact with the modifiers of this invention differs from regular viscose yarn in five other respects: (1) the density appears to be higher than that of normal viscose yarns of the same orientation; (2) the yarns of this invention behave differently when fibrillated in the presence of water in that they do not break up into fine longitudinal fibrils as do yarns from unmodified viscose; (3) the yarns of this invention have higher lateral order than do yarns from unmodified viscose; (4) the yarns dye more rapidly than yarns from unmodified viscose; (5) the yarns of this invention have considerably lower secondary swelling (water take-up by dried yarns). The yarns of this invention have a lateral order of less than 35, i. e., about 5 to about 35; a secondary swelling of less than 85%, i. e., about 65% to about 85%; and less than about 40% core, the skin varying from about 60% to about 100%. As the amount of skin approaches 65 100%, the amount of core becomes negligible and the diffuse boundary is difficult to bring out by the dyeing technique, the negligible-core yarns, obtained, for example, by Example III or X and described and claimed by this invention, still being characterized by lateral orders, secondary swellings, etc. which distinguish them from other yarns as pointed out above. In the following Table IB, the physical characteristics of yarns from modified viscose in comparison with other 70 known yarns are shown.

Table IB

| Fiber   | Skin             |              | Cross-Section |                | Fibrillation Resistance | Density | Secondary Swelling | Dye Absorption Rate, min. | X-Ray Data    |             | Fatigue Resistance, hrs. | Tenacity, g. per denier |     |
|---|------------------|--------------|---------------|----------------|-------------------------|---------|--------------------|---------------------------|---------------|-------------|--------------------------|-------------------------|-----|
|   | Per Cent Approx. | Boundary     | Crenulations  | Contour        |                         |         |                    |                           | Lateral Order | Orientation |                          | Dry                     | Wet |
| 1 From unripened viscose; benzyltrimethylammonium hydroxide — modified Example I. | 60               | Diffuse      | None          | Oval to Round. | Great                   | 1.92    | 72                 | 8                         | 18            | 7.4         | 50+                      | 3.8                     | 2.7 |
| 2 Control; unripened, unmodified viscose.   | 30-40            | Sharp        | Many          | Irregular      | -----                   | -----   | 86                 | -----                     | 13            | 7.0         | -----                    | 3.7                     | 2.2 |
| 3 Control; ripened, unmodified viscose.   | 60               | do           | do            | do             | -----                   | -----   | 93                 | -----                     | 13            | 6.0         | -----                    | 3.4                     | 2.2 |
| 4 "Cordura" 237 (tire cord yarn).   | 50               | do           | do            | do             | Little                  | 1.23    | 88                 | -----                     | 29            | 8.1         | 25                       | 3.7                     | 2.4 |
| 5 Textile "Cordura".  | 40               | do           | do            | do             | -----                   | -----   | 109                | 15                        | 34            | 6.0         | -----                    | 2.5                     | 1.5 |
| 6 "Cordura" 540 (experimental).   | 60               | Fairly Sharp | do            | do             | Little                  | 1.17    | 97                 | 11                        | 20            | 7.5         | 45                       | 3.9                     | 2.5 |
| 7 Lilienfeld yarn.  | None             | -----        | None          | Round          | -----                   | -----   | -----              | -----                     | 11            | 7.0         | -----                    | 3.2                     | 1.4 |
| 8 "Fiber D" (U. S. P. 2,249,745).   | None             | -----        | do            | do             | -----                   | -----   | 100+               | -----                     | 33            | 2.0         | -----                    | 1.1                     | 0.6 |
| 9 Bemberg yarn.   | None             | -----        | do            | do             | -----                   | -----   | 98                 | 0.7                       | 44            | 5.0         | -----                    | 1.8                     | 0.8 |
| 10 Standard textile yarn  | 20-40            | Sharp        | Many          | do             | -----                   | -----   | -----              | -----                     | 38            | 3.0         | -----                    | 2.0                     | 1.0 |

In the above table, the dye absorption rate refers to the time in minutes required for the absorption of 50% of the dye by 5 grams of yarn from a bath consisting of 250 grams of water, 0.1 gram of Pontamine Fast Green 5 BL and 1.5 g. of sodium sulfate at 85° C.

The X-ray data are measured photometrically from flat plate diffraction patterns, the distance between the specimen and the film being 5 cm. The lateral order, which is a measure of crystallinity, is given by the expression

$$\frac{(I_1 - I_m)}{I_1} 100$$

where  $I_1$  is the 101 interference intensity and  $I_m$  is the minimum intensity between the 101 and the 101 interferences. The orientation is given by the expression.

$$\frac{I_3}{I_{90(3)}}$$

where  $I_3$  is the 002 interference intensity and  $I_{90(3)}$  is the same at 90° from the equator.

EXAMPLE II

A 7-6 viscose (7% cotton linter cellulose-6% total sodium hydroxide) modified with 1.5 millimoles of benzyltrimethylammonium hydroxide per 100 grams of viscose is prepared and spun in the manner described in Example I using the same sulfuric acid-sodium sulfate-zinc sulfate (8-14-15) coagulating and regenerating bath. The yarns are washed, slashed, and plied to a 275/3/3 construction. Three strands of 275 denier yarn are plied together and then three such bundles are combined to make the cord. Yarn and cord properties are given in Table II along with those for regular viscose controls. It will be noted that the yarn from the modified, green viscose shows large improvements in yarn and cord strength and fatigue resistance of the cord over yarn produced from normally ripened viscose spun under identical conditions.

Table II

| Yarn Properties           | Unripened Modified | Ripened Unmodified |
|---------------------------|--------------------|--------------------|
| 30 Ten. g./d. Dry         | 3.80               | 3.35               |
| Ten. g./d. Wet            | 2.75               | 2.57               |
| Ten. g./d. Loop           | 2.98               | 2.95               |
| Elong. Per Cent Dry       | 10.3               | 9.2                |
| Elong. Per Cent Wet       | 22.7               | 24.4               |
| Elong. Per Cent Loop      | 6.8                | 6.6                |
| Gel Swelling              | 2.6                | 3.1                |
| "D" Value, in inches      | 7.0                | 3.0                |
| Cord Properties           |                    |                    |
| 40 Conditioned Ten. g./d. | 3.51               | 3.07               |
| Oven-dry Ten. g./d.       | 3.98               | 3.46               |
| Fatigue Hours             | >48                | 39                 |

EXAMPLE III

A 7-6 viscose modified with 1.5 millimoles of benzyltrimethylammonium hydroxide per 100 grams of viscose is prepared and spun and the yarns are processed in the manner described in Example I. In this case, however, the coagulating bath is 8.0-23-4 ( $H_2SO_4-Na_2SO_4-ZnSO_4$ ). The physical properties of the yarns from the unripened modified viscose are much better than for accompanying controls from normally ripened viscose, as is shown in Table III.

Table III

| Yarn Properties        | Unripened Modified | Ripened Unmodified |
|------------------------|--------------------|--------------------|
| 55 Ten. g./d. Dry      | 3.88               | 3.45               |
| Ten. g./d. Wet         | 2.72               | 2.33               |
| Ten. g./d. Loop        | 2.97               | 2.43               |
| 60 Elong. Per Cent Dry | 7.8                | 6.4                |
| Elong. Per Cent Wet    | 20.2               | 20.7               |
| Elong. Per Cent Loop   | 5.3                | 3.7                |
| Gel Swelling           | 2.61               | 3.4                |
| "D" Value, inches      | 6.0                | 2.5                |

EXAMPLE IV

Cotton linters viscose similar to that described in Example II is spun into filaments using all conditions for producing and processing as in Example I except that the acidity of the high zinc bath is increased from 8 to 9½%  $H_2SO_4$ . The properties of the yarns as well as those of yarns from unmodified ripened and unripened control viscoses are shown in Table IV. It will be seen that the use of the modified unripened viscose at this higher bath acidity gives lower

gel swelling and improved properties. The high spinning speeds desirable in commercial practice require relatively high bath acidity, which in turn means a certain sacrifice in yarn properties because of the increased gel swelling. As shown in this example, it is possible through modification of viscose to employ high spinning speeds at high acidity without the disadvantage just mentioned.

Table IV

| Yarn Properties           | Unripened Modified | Unripened Unmodified | Ripened Unmodified |
|---------------------------|--------------------|----------------------|--------------------|
| Ten. g./d. Dry.....       | 4.0                | 3.55                 | 3.45               |
| Ten. g./d. Wet.....       | 2.81               | 2.0                  | 2.20               |
| Ten. g./d. Loop.....      | 2.46               | 2.20                 | 1.93               |
| Elong. Per Cent Dry.....  | 3.8                | 7.7                  | 8.0                |
| Elong. Per Cent Wet.....  | 21.5               | 18.6                 | 21.3               |
| Elong. Per Cent Loop..... | 4.0                | 5.2                  | 4.1                |
| Gel Swelling.....         | 2.74               | 3.12                 | 3.46               |
| "D" Value, in inches..... | 4.5                | 1.5                  | 1.5                |

## EXAMPLE V

Two viscoses made from 7% cotton linters, 6% sodium hydroxide, and 35% carbon bisulfide and containing (1) 0.68 millimole of tetraethylammonium hydroxide per 100 grams of viscose and (2) 0.68 millimole of tetraethylammonium bromide per 100 grams of viscose are spun in the unripened state into filaments, using an 8-14-15 ( $H_2SO_4-Na_2SO_4-ZnSO_4$ ) bath. The gel swelling values are reduced and the properties of the yarns are improved as in the case of benzyltrimethylammonium hydroxide. The properties of these yarns are compared with those of yarns from unripened, unmodified viscose in Table V below.

Table V

| Yarn Properties           | Unripened+<br>( $C_2H_5$ ) <sub>4</sub> NOH | Unripened+<br>( $C_2H_5$ ) <sub>4</sub> NBr | Unripened<br>Unmodified |
|---------------------------|---|---|-------------------------|
| Ten. g./d. Dry.....       | 3.60  | 3.32  | 3.60                    |
| Ten. g./d. Wet.....       | 2.65  | 2.72  | 1.99                    |
| Ten. g./d. Loop.....      | 2.76  | 3.11  | 2.74                    |
| Elong. Per Cent Dry.....  | 7.5   | 8.3   | 8.5                     |
| Elong. Per Cent Wet.....  | 22.4  | 22.3  | 18.5                    |
| Elong. Per Cent Loop..... | 4.9   | 5.8   | 6.7                     |
| Gel Swelling.....         | 2.56  | 2.67  | 3.11                    |
| "D" Value, in inches..... | 3.5   | 3.5   | 1.7                     |

## EXAMPLE VI

A cotton linter viscose containing 7% cellulose, 6% total sodium hydroxide, and 2.0 millimoles per 100 grams of tetramethylammonium chloride per 100 parts of viscose is prepared as described in Example I. The viscose is spun in an unripened state in a sulfuric acid-sodium sulfate-zinc sulfate (8-14-15) bath and all conditions of Example I for spinning and processing are used with the exception that 100% instead of 80% stretch is employed in the secondary bath. The table below shows the improvement in yarn properties and gel swelling obtained with this modifier.

Table VI

| Yarn Properties           | Unripened+<br>( $CH_3$ ) <sub>4</sub> NCl | Unripened<br>Unmodified |
|---------------------------|---|-------------------------|
| Ten. g./d. Dry.....       | 3.95                                      | 3.79                    |
| Ten. g./d. Wet.....       | 2.80                                      | 2.38                    |
| Ten. g./d. Loop.....      | 2.78                                      | 2.74                    |
| Elong. Per Cent Dry.....  | 6.7                                       | 7.0                     |
| Elong. Per Cent Wet.....  | 19.5                                      | 16.8                    |
| Elong. Per Cent Loop..... | 4.1                                       | 4.3                     |
| Gel Swelling.....         | 2.87                                      | 3.12                    |
| "D" Value, in inches..... | 3.5                                       | 1.7                     |

## EXAMPLE VII

Unripened 7-8 viscose containing 1.7 millimoles of phenyltrimethylammonium hydroxide per 100 grams of viscose is spun into an 8-14-15 ( $H_2SO_4-Na_2SO_4-ZnSO_4$ ) bath and the yarn is stretched and processed as in Example I. The reduction in gel swelling and neutralization rates (increased "D" value) and the improved yarn properties of the non-crenulated fiber thus obtained are shown in Table VII below:

Table VII

| Yarn Properties           | Unripened Modified | Ripened Unmodified |
|---------------------------|--------------------|--------------------|
| Ten. g./d. Dry.....       | 3.87               | 3.60               |
| Ten. g./d. Wet.....       | 2.78               | 1.99               |
| Ten. g./d. Loop.....      | 3.09               | 2.74               |
| Elong. Per Cent Dry.....  | 8.0                | 8.5                |
| Elong. Per Cent Wet.....  | 22.2               | 18.5               |
| Elong. Per Cent Loop..... | 5.5                | 6.7                |
| Gel Swelling.....         | 2.7                | 3.12               |
| "D" Value, in inches..... | 3.3                | 1.7                |

## EXAMPLE VIII

Cotton linters viscose containing 7% cellulose, 6% total alkali as sodium hydroxide, and 1.7 millimoles of tetraethylammonium hydroxide per 100 grams of viscose is prepared as described in Example I. In this case, however, the viscose is ripened as is done for normal viscose to a salt index of 5.0 (xanthate surfur 1.1%). It is then spun into filaments under the conditions of Example I except that 6% instead of 8% sulfuric acid is used in the sulfuric acid-sodium sulfate-zinc sulfate bath. The same large reduction in gel swelling and neutralization rates are observed with this ripened viscose as with the green viscoses of the preceding examples. In addition, the wet strength is increased and filament contours are changed as in the case of filaments from green viscose modified with non-surface-active quaternary ammonium compounds. Table VIII below shows the yarn properties as compared with a control yarn.

Table VIII

| Yarn Properties           | Unripened Modified | Ripened Unmodified |
|---------------------------|--------------------|--------------------|
| Ten. g./d. Dry.....       | 3.64               | 3.18               |
| Ten. g./d. Wet.....       | 2.75               | 2.32               |
| Ten. g./d. Loop.....      | 2.92               | 2.43               |
| Elong. percent Dry.....   | 8.0                | 10.5               |
| Elong. percent Wet.....   | 24.0               | 22.4               |
| Elong. percent Loop.....  | 5.0                | 5.5                |
| Gel Swelling.....         | 2.0                | 3.1                |
| "D" Value, in inches..... | 4.5                | 3.0                |

## EXAMPLE IX

Cotton linters viscose containing 7% cellulose, 6% total caustic, and 2.8 millimoles of tetramethylammonium chloride per 100 grams of viscose is prepared and ripened to a salt index of 5.0 as is normally done for regular viscose, and then spun into filaments using all the conditions of Example I for collection and processing with the exception that a 9-23-4 ( $H_2SO_4-Na_2SO_4-ZnSO_4$ ) bath is used instead of an 8-14-15 bath. A considerable decrease in gel swelling and increase in "D" value are obtained, which are reflected in a measurable increase in wet strength of the yarn. The character of the filament is changed in the same manner as noted with other modifiers and unripened viscoses. Table IX below shows the yarn properties as compared with a control yarn.

11  
Table IX

| Yarn Properties           | Unripened Modified | Ripened Unmodified |
|---------------------------|--------------------|--------------------|
| Ten. g./d. Dry.....       | 3.47               | 3.45               |
| Ten. g./d. Wet.....       | 2.50               | 2.23               |
| Ten. g./d. Loop.....      | 2.40               | 2.43               |
| Elong. percent Dry.....   | 6.5                | 6.4                |
| Elong. percent Wet.....   | 22.5               | 20.7               |
| Elong. percent Loop.....  | 3.9                | 3.7                |
| Gel Swelling.....         | 2.61               | 3.40               |
| "D" Value, in inches..... | 4.5                | 2.5                |

## EXAMPLE X

Unmodified cotton linters viscose containing 7% cellulose and 6% total caustic is prepared as described in Example I. It is spun in the unripened state into a coagulating bath containing 8% sulfuric acid, 23% sodium sulfate, 4% zinc sulfate, and 0.2% benzyltrimethylammonium chloride, using the conditions of Example I for collection and processing of yarn. The properties of the yarn are compared in Table X below with those of control spun into an identical bath except that the quaternary ammonium compound is omitted. The same large reduction in gel swelling, increase in neutralization rates, modification of filament, contour, and improvement in strength are observed as when the modifying agent is added to the viscose.

Table X

| Yarn Properties           | Modified Bath | Unmodified Bath |
|---------------------------|---------------|-----------------|
| Ten. g./d. Dry.....       | 3.7           | 3.6             |
| Ten. g./d. Wet.....       | 2.6           | 2.1             |
| Ten. g./d. Loop.....      | 2.7           | 2.6             |
| Elong. Percent Dry.....   | 7.6           | 8.1             |
| Elong. Percent Wet.....   | 23.0          | 20.0            |
| Elong. Percent Loop.....  | 5.0           | 5.4             |
| Gel Swelling.....         | 2.7           | 3.3             |
| "D" Value, in inches..... | 3.5           | 2.2             |

## EXAMPLE XI

A 7-6 viscose is prepared as in Example I except that the modifier is tetraethanolammonium hydroxide,  $(\text{OHCH}_2\text{CH}_2)_4\text{N}-\text{OH}$ , used in concentration of 1.5 millimoles per 100 grams of viscose. The viscose is then spun in the unripened state, using the conditions described in Example I. Similar improvements are observed, as shown in the following table.

Table XI

| Yarn Properties           | Unripened Modified | Unripened Unmodified |
|---------------------------|--------------------|----------------------|
| Ten. g./d. Dry.....       | 3.84               | 3.6                  |
| Ten. g./d. Wet.....       | 2.72               | 1.99                 |
| Ten. g./d. Loop.....      | 2.84               | 2.74                 |
| Elong. Percent Dry.....   | 7.3                | 8.0                  |
| Elong. Percent Wet.....   | 20.4               | 18.5                 |
| Elong. Percent Loop.....  | 9.6                | 6.7                  |
| Gel Swelling.....         | 2.75               | 3.11                 |
| "D" Value, in inches..... | 6.5                | 1.8                  |

## EXAMPLE XII

In copending application, filed by N. L. Cox on March 22, 1946, with Serial No. 656,478, it is shown that addition of small amounts of alkali trithiocarbonate to unripened viscose permits spinning the unripened viscose to give fibers with properties comparable or superior to those of fibers spun from normally ripened viscose. It has now been found that the alkali trithiocarbonate modification can be combined with further advantage with the treatment described in the preceding examples.

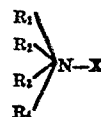
To a 7-6 viscose prepared as in Example I is added 1.5 millimoles of benzyltrimethylammonium hydroxide per 100 grams of viscose and 0.44% of sodium trithiocarbonate. The viscose is spun in the unripened state under the conditions of Example I, using a sulfuric acid-sodium sulfate-zinc sulfate (8-15-15) bath. It will be seen from the table below that the "D" value of this viscose having a combination of modifiers is far greater than that of viscose having only benzyltrimethylammonium hydroxide, in the same amount, as modifier. Furthermore, the "D" value is at least equal and, in general, superior to that of a viscose ripened to the same trithiocarbonate content as the modified, green viscose and containing the same amount of quaternary ammonium compound modifier.

Table XII

| Yarn Properties                               | Unripened Modified with $\text{Na}_2\text{CS}_3$ and— | Unripened Modified with— | Ripened Modified with— |
|---|---|--------------------------|------------------------|
|   | Benzyltrimethylammonium Hydroxide                     |                          |                        |
| Percent $\text{Na}_2\text{CS}_3$ , total..... | 1.25  | 0.6                      | 1.35                   |
| Ten. g./d. Dry.....                           | 3.82  | 3.88                     | 3.82                   |
| Ten. g./d. Wet.....                           | 2.60  | 2.72                     | 2.48                   |
| Ten. g./d. Loop.....                          | 2.92  | 2.92                     | 2.44                   |
| Elong. Percent Dry.....                       | 7.8   | 7.8                      | 7.9                    |
| Elong. Percent Wet.....                       | 20.3  | 20.2                     | 18.2                   |
| Elong. Percent Loop.....                      | 5.1   | 5.2                      | 4.3                    |
| Gel Swelling.....                             | 2.76  | 2.61                     | 2.78                   |
| "D" Value, in inches.....                     | 11.0  | 6.0                      | 11.0                   |

The practical significance of the synergistic effect in green viscose between alkali trithiocarbonate modifier and quaternary ammonium compound modifier lies in the fact that the rate of neutralization of the filament is susceptible of greater variation and, hence, is more flexible, permitting closer adjustment to the desired spinning speed. Moreover, it is possible to replace part of the relatively expensive quaternary ammonium compound with cheap sodium trithiocarbonate.

The modifying agents suitable for the purpose of this invention are quaternary ammonium compounds having the gross formula



wherein X is a hydroxyl group or an anion having no surface activity, e. g., the chloride, bromide, iodide, sulfate, bisulfate, acetate, etc., anions, and the radicals  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , are organic groups having not more than four aliphatic carbons, at least three of these radicals being completely aliphatic and the fourth one, when aromatic, containing not more than one aromatic (benzene) nucleus. All R groups may be aliphatic and in that instance they may be alike or different. A chemical structure involving only short aliphatic chains or only one aromatic nucleus is intimately connected with the absence of surface-active properties in the modifying agents which has been found essential if the objects of the invention are to be achieved. More specifically, the quaternary ammonium compounds contemplated here are those which do not, in concentrations of 0.1%, lower the surface tension of distilled water at 25° C. by more than about 6 dynes per centimeter. The following Table XIII shows the surface tension of 0.1% aqueous solutions of a number of quater-

nary ammonium compounds. The first six members of the table are short-chain compounds, i. e., compounds having no aliphatic chain longer than four carbons or no aromatic chain longer than one benzene nucleus. It will be noted that they have substantially no surface tension-lowering effect. In comparison, it will be seen that surface activity becomes appreciable with a six to eight carbon chain, and is very high with compounds having twelve or more carbons in a chain.

Table XIII

| Modifier                                  | Surface Tension, dynes per cm. | Difference from Water, dynes per cm. |
|---|--------------------------------|--------------------------------------|
| Tetramethylammonium chloride              | 72.3                           | 0.3                                  |
| Tetraethylammonium hydroxide              | 66.8                           | 5.8                                  |
| Tetrahydroxyethylammonium hydroxide       | 67.5                           | 5.1                                  |
| Tetrabutylammonium iodide                 | 67.4                           | 5.2                                  |
| Phenyltrimethylammonium hydroxide         | 71.4                           | 1.2                                  |
| Benzyltrimethylammonium chloride          | 72.5                           | 0.1                                  |
| Hexyltrimethylammonium bromide            | 63.8                           | 8.8                                  |
| Octyltrimethylammonium chloride           | 64.0                           | 8.6                                  |
| Dodecyltrimethylammonium chloride         | 37.7                           | 34.0                                 |
| Hexadecylbenzyltrimethylammonium chloride | 37.7                           | 34.0                                 |
| Water                                     | 72.6                           |                                      |

The critical importance, for the success of the method here described, of using materials essentially devoid of surface tension-lowering properties is effectively demonstrated by substituting for the short-chain quaternary ammonium compounds a similar material having a long aliphatic chain and, therefore, surface-active. For example, the use in viscose of dodecyltrimethylammonium chloride at a concentration (0.38 millimole per 100 grams of viscose or 0.1%) comparable on a weight basis with those used in the above examples produces no appreciable decrease in gel swelling, no increase in "D" value, and no change in the physical characteristics of the yarn, e. g., in filament cross section. Increasing the concentration to one comparable on a molar basis with that of the examples (i. e., up to 1.3 millimoles per 100 grams or 0.33%) only makes matters worse since it causes an excessive increase in the viscosity of the viscose coupled with extreme difficulty of deaeration, and gives yarn having inferior properties as compared to control yarn.

In terms of chemical structure, the preferred modifiers for use in this invention are those in which all four organic groups attached to the nitrogen atom are hydrocarbon groups or hydroxyl-substituted hydrocarbon groups and in which the radical X is hydroxyl or halogen of atomic weight above 19, i. e., chlorine, bromine, or iodine. The most useful modifiers are the quaternary ammonium hydroxides having a total of not more than ten carbon atoms in the molecule and in which all organic groups are hydrocarbon or hydroxyl-substituted hydrocarbon. An obvious requirement of the modifying agents is that they be soluble in the viscose or in the coagulating bath, i. e., in alkaline or acidic media, to the extent of at least 0.5%. Furthermore, they must be substantially inert chemically toward and unaffected by the components of the viscose and of the coagulating bath. Suitable agents which may be mentioned in addition to those used in the examples are tetraethylammonium bromide, tetramethylammonium iodide, tetrapropylammonium hydroxide, tetrabutylammonium chloride, tributylpropylammonium hydroxide, tri(beta-hydroxyethyl)-methylammo-

nium hydroxide, tributyl(beta-hydroxyethyl-ammonium iodide, etc.

As has been shown, the non-surface-active quaternary ammonium compounds may be used either in the viscose or in the coagulating-regenerating bath. The agents may also be added to both the viscose and the bath in equal or different amounts, the total concentration being generally not more than about 10.0 millimoles per 100 grams of total solvent. In the latter event, the agent added to the bath may be the same as or different than the agent added to the viscose. For effective results, there should be used at least 0.5 millimole of agent per 100 grams of viscose or bath (the desirable concentration is about 0.9 and about 3.0 millimoles per 100 grams. In terms of weight percent basis, there should be used between about 0.04% and about 0.3% of modifying agent, based on either the viscose or bath. The optimum concentration for any given agent depends on its effectiveness and on its molecular weight. It also depends to some extent on process variables such as the spinning speed, since at the high spinning speeds used in industrial practice, less agent is desirable than at lower spinning speeds, for the reason that the rate of neutralization of the filament should be retarded only to the extent compatible with complete coagulation during the short time the filament is in contact with the coagulating bath. Determination of the optimum concentration of the quaternary ammonium compound is a matter of simple experimentation for those skilled in the art. In this connection it should be pointed out that with ripened viscose there need be used somewhat less modifying agent than with unripened viscose, probably because the increase in alkali trithiocarbonate concentration which accompanies the ripening step tends to reinforce the effect of the modifying agent.

The viscose used in the process of the invention may be of a variety of types; for example, it may be from wood pulp, cotton linters, mixtures of the two, or even other types of cellulose. The composition of the viscose may also be varied widely. For example, it may have a cellulose content of from 4 to 10% or even more and an alkali content of from 4 to 8% or more. The standard viscoses of the industry, i. e., those having between 5 and 7% cellulose and between 4-6% alkali, are preferably used. The amount of carbon disulfide used in xanthation can be from 25-50% (based on the recoverable bone-dry cellulose). It has been found that higher than normal xanthate sulfur contents (higher salt indices) can be used in the viscose when the short-chain quaternary ammonium compounds described herein are added and there appears to be an advantage in stretchability and level of yarn properties if salt indices higher than 5 are used. It is necessary to use 30% or greater amounts of carbon disulfide to obtain salt indices of 5 or over in unripened viscoses. Thus, one of the chief advantages of the invention is that unripened or partially ripened viscoses may be used, with the result that the ripening time and space now required in viscose plants may be eliminated or substantially reduced. A very useful embodiment of the invention is that illustrated in Example XII, wherein unripened viscose is modified with a combination of a non-surface-active quaternary ammonium



compound and added alkali trithiocarbonate. In such a case, an unexpected synergistic effect is observed as regards the neutralization rate and the yarns are of remarkably high quality. As specified in copending application Serial Number 656,478, already referred to, the quantity of alkali trithiocarbonate (e. g., sodium or potassium trithiocarbonate) to be added to the green viscose need only be sufficient to bring the total trithiocarbonate content to between about 1% and about 3%, based on the viscose, which means in general that the amount added is between 0.2% and 2.25% of the weight of the viscose.

While the use of unripened viscose is of special interest in the process of this invention, it has been shown (Examples VIII and IX) that notable improvements in yarn quality are also obtained with normally ripened viscose, thus making the process directly applicable to existing plant practice.

The spinning baths suitable for use in the invention contain sulfuric acid, sodium sulfate, and zinc sulfate. Zinc sulfate is an essential component of the spinning bath since, in its absence, the quaternary ammonium compounds have no effect on spinning and yarn properties. If desired, additional salts of divalent metals known to reinforce or supplement the action of zinc sulfate may be used, such as ferrous sulfate, manganese sulfate, nickel sulfate, or chromic sulfate. Ferrous sulfate is particularly useful. Preferably, the spinning bath contains from 4 to 12% of sulfuric acid, from 13 to 25% of sodium sulfate, and from 1 to 15% of zinc sulfate, optionally including between 0.8 and 6%, and preferably between 1% and 5%, of ferrous sulfate. The optimum quantity of zinc sulfate from the standpoint of practical spinning speed appears to be 3 to 5%. With the addition of quaternary ammonium salts to viscose or spinning baths, it is possible to obtain excellent yarns using bath acidities in the upper range under which conditions normal, unmodified viscoses give yarns of decreased quality. It is also possible to use in this invention the long chain quaternary ammonium compounds referred to above and at low concentrations in their usual capacity as incrustation-preventing agents. The temperature range of best spinnability is from 40 to 65° C. On the basis of available data, it is desirable to have the bath acidity and temperatures as low as is practical for a given spinning speed in order to get optimum filament structure and yarn properties. Each of the above concentrations should be adjusted to each other and to the composition of the viscose. It is desirable to use as high a total solids content as possible in the coagulating bath to give the highest degree of gel shrinkage and improved stretchability.

The filaments may be given a long travel of 130-250 inches in the primary bath by means of a multiple roller setup which gradually applies tension to the traveling filaments and thereby orients them while they are still plastic. The preferred method, however, is to apply a part or all of the stretch beyond the primary bath in a secondary bath or to use a combination of air and hot bath stretch. The secondary bath may consist simply of water or of dilute (1-3%) sulfuric acid, or it may have the same composition as the coagulating bath but at a greater dilution, e. g., one-fourth of the concentration of the coagulating bath. The temperature of the secondary bath is preferably between 50 and 100° C. Stretches of 80-100% are preferred for pro-

ducing high tenacity yarn and 20-30% for textile type yarns. The bobbin process has been used in the examples, but it is immaterial whether spinning is by bobbin, bucket, or continuous processes. The yarn cake is washed free of acid and salt and then dried under tension. If preferred, it may be twister- or slasher-dried to enable the dry elongation of the finished product to be controlled. When using the two-bath spinning system, the preferred procedure is to draw off the freshly coagulated gel yarn with a feed wheel speed equal to or less than the jet velocity and to apply all of the stretch between positively driven rollers traveling at different speeds. The thread can be given a travel of 10-50 inches in the secondary bath of hot water or dilute bath. As mentioned above, the amount of stretch applied depends on the properties desired for the yarn.

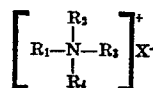
On the basis of available data, it is thought probable that the mechanism by which quaternary ammonium compounds influence the spinning process is through interaction with zinc sulfate on the one hand and with the sodium trithiocarbonate of the viscose on the other hand. It has not yet been possible to determine whether this effect on filament formation is accomplished through (1) buffer action, (2) transient formation of insoluble complexes, which might exercise some control on the porosity of the initial skin which is set up, (3) ionbridge formation, or (4) other colloidal effects.

The novel and improved yarns obtainable through the process of this invention can, in general, be used instead of regular regenerated cellulose fibers for any purposes where the latter are finding applications, more particularly in the textile and tire cord industries.

Any departure from the above description which conforms to the present invention is intended to be included within the scope of the claims.

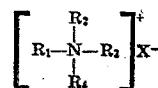
I claim:

1. A method of producing regenerated cellulosic structures which comprises the step of spinning a viscose solution in a spinning bath comprising an aqueous solution of sulfuric acid containing from 1% to 15% zinc sulfate, the said spinning being conducted in the presence of about 0.5 to about 10.0 millimoles per 100 grams of one of said solutions of a water-soluble quaternary ammonium compound of the formula



wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups contain only aliphatic carbon atoms and the fourth of the said groups contains no more than one phenyl radical and where  $X^-$  is an anion having substantially no surface activity.

2. A method of producing regenerated cellulosic structures which comprises the step of spinning viscose in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate together with, per 100 grams of bath, about 0.5 to about 10.0 millimoles of a water-soluble quaternary ammonium compound of the formula

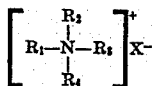


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wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are aliphatic radicals, each of the said radicals containing no more than 4 carbon atoms and  $X^-$  is an anion having substantially no surface activity.

3. A process as defined in claim 2 in which the said structures are passed into a second bath and subjected to a stretching treatment in said second bath.

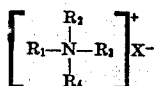
4. A method of producing regenerated cellulosic structures which comprises the step of spinning viscose in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate, the said viscose containing, per 100 grams of viscose, about 0.5 to about 10.0 millimoles of a water-soluble quaternary ammonium compound of the formula



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are aliphatic radicals each of the said radicals containing no more than 4 carbon atoms and  $X^-$  is an anion having substantially no surface activity.

5. A process as defined in claim 4 in which the said structures are passed into a second bath and subjected to a stretching treatment in said second bath.

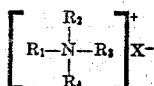
6. A method of producing regenerated cellulosic structures which comprises the step of spinning viscose in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate together with, per 100 grams of bath, about 0.9 to about 3.0 millimoles of a water-soluble quaternary ammonium compound of the formula



wherein  $R_1$ ,  $R_2$ , and  $R_3$  are aliphatic radicals, each of the said radicals containing no more than 4 carbon atoms, the radical  $R_4$  containing no more than 4 aliphatic carbon atoms and no more than 1 phenyl radical, and  $X^-$  is an anion having substantially no surface activity.

7. A process as defined in claim 6 in which the said structures are passed into a second bath and subjected to a stretching treatment in said second bath.

8. A method of producing regenerated cellulosic structures which comprises the step of spinning viscose in an aqueous sulfuric acid spinning bath containing from 1% to 15% zinc sulfate, the said viscose containing, per 100 grams of viscose, about 0.9 to about 3.0 millimoles of a water-soluble quaternary ammonium compound of the formula



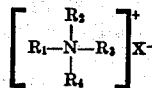
wherein  $R_1$ ,  $R_2$  and  $R_3$  are aliphatic radicals, each of the said radicals containing no more than 4 carbon atoms, the radical  $R_4$  contains no more than 4 aliphatic carbon atoms and no more than 1 phenyl radical, and  $X^-$  is an anion having substantially no surface activity.

9. A process as defined in claim 8 in which the said structures are passed into a second bath and subjected to a stretching treatment in said second bath.

10. A method of producing regenerated cellulosic structures which comprises the step of spinning viscose containing a water-soluble trithiocarbonate in addition to that formed during xanthation in an aqueous sulfuric acid bath con-

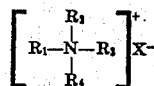
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taining 1% to 15% zinc sulfate together with about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of bath, the said quaternary ammonium compound corresponding to the formula



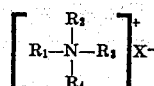
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and whereas  $X^-$  is an anion having substantially no surface-activity.

11. A process which comprises incorporating in viscose which contains a water-soluble trithiocarbonate in addition to that formed during xanthation about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of viscose and extruding the resultant viscose into a coagulating bath comprising an aqueous solution of sulfuric acid and 1% to 15% zinc sulfate, the said quaternary ammonium compound corresponding to the formula



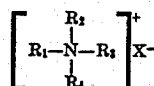
wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and wherein  $X^-$  is an anion having substantially no surface-activity.

12. A process according to claim 11 in which the said coagulating bath also contains about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of bath, the said quaternary ammonium compound corresponding to the formula



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and where  $X^-$  is an anion having substantially no surface-activity.

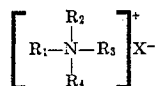
13. A process which comprises incorporating in viscose containing an alkali metal trithiocarbonate in addition to that formed during xanthation about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of viscose, extruding the resultant viscose into a coagulating bath comprising an aqueous solution of 4% to 12% sulfuric acid, 13% to 25% sodium sulfate and 1% to 15% zinc sulfate, the said quaternary ammonium compound corresponding to the formula



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one

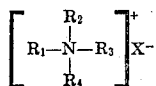
phenyl radical and wherein  $X^-$  is an anion having substantially no surface-activity.

14. A process according to claim 13 in which the coagulating bath contains about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of bath, the said quaternary ammonium compound corresponding to the formula



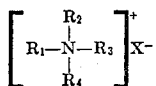
wherein  $R_1, R_2, R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and wherein  $X^-$  is an anion having substantially no surface-activity.

15. An aqueous sulfuric acid spinning bath for the spinning of regenerated cellulosic structures from viscose, said bath containing from 1% to 15% zinc sulfate together with about 0.5 to about 10.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of bath, the said quaternary ammonium compound corresponding to the formula



wherein  $R_1, R_2, R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and wherein  $X^-$  is an anion having substantially no surface-activity.

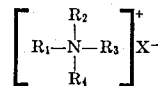
16. An aqueous sulfuric acid bath for the spinning of regenerated cellulosic structures from viscose, said bath containing from 4% to 12% sulfuric acid, 13% to 25% sodium sulfate, 1% to 15% zinc sulfate and about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of bath, the said quaternary ammonium compound corresponding to the formula



wherein  $R_1, R_2, R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and wherein  $X^-$  is an anion having substantially no surface-activity.

17. An aqueous sulfuric bath for the spinning of regenerated cellulosic structures from viscose, said bath containing from 4% to 12% sulfuric acid, 13% to 25% sodium sulfate, 1% to 15% zinc sulfate, 1% to 5% ferrous sulfate and about 0.9 to about 3.0 millimoles of a water-soluble, quaternary ammonium compound per 100 grams of

bath, the said quaternary ammonium compound corresponding to the formula



wherein  $R_1, R_2, R_3$  and  $R_4$  are organic groups which contain no more than four aliphatic carbon atoms, at least three of the said groups containing only aliphatic carbon atoms, and the fourth of the said groups containing no more than one phenyl radical and wherein  $X^-$  is an anion having substantially no surface-activity.

18. A filament of regenerated cellulose having a smooth surface, showing no appreciable crenulation and having a core surrounded by a skin, the ratio of the cross-sectional area of the skin to the core being greater than one and the boundary therebetween being diffuse.

19. A filament of regenerated cellulose having a smooth surface, and showing no appreciable crenulation, being composed of about 40% core surrounded by about 60% skin, the boundary therebetween being diffuse.

20. A filament in accordance with claim 18 characterized by a lateral order of about 18.

21. A process in accordance with claim 1 in which the said quaternary ammonium compound is benzyltrimethylammonium hydroxide.

22. A process in accordance with claim 1 in which the said quaternary ammonium compound is tetraethylammonium hydroxide.

23. A process in accordance with claim 1 in which the said quaternary ammonium compound is tetramethylammonium hydroxide.

NORMAN LOUIS COX.

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**Certificate of Correction**

Patent No. 2,536,014

December 26, 1950

**NORMAN LOUIS COX**

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 8, for the word "or" read *of*; column 4, lines 18 and 21, for "the 'D' value" read *the "D" value*; line 23, same column, for "the D" value" read *the "D" value*; line 26, for "increased 'D' value" read *increased "D" value*; line 49, for "viscos" read *viscose*; column 6, line 13, for "dif-fused" read *diffuse*; columns 5 and 6, Table IA, in the heading to the last portion thereof, for " $-\text{Na}_2\text{SO}_2-$ " read  $-\text{Na}_2\text{SO}_4-$ ; columns 7 and 8, Table IB, first line under the heading "Density" for "1.92" read *1.29*; same line, under the heading, "Orientation" for "7.4" read *7.0*; column 7, line 45, for "101" read *10 $\bar{1}$* ; line 74, for "warn" read *yarn*; column 8, Table III, column 9, Tables IV, V, and VI, under the heading "Yarn Properties", seventh line, respectively, for "Gel Swelling" read *Gel Swelling g.*; column 10, Table VII, third column thereof, for "Ripened" read *Unripened*; Table VIII, second column, for "Unripened" read *Ripened*; column 12, line 7, for "(8-15-15)" read *(8-14-15)*; column 14, line 1, for "beta-hydroxyethyl-am-" read *beta-hydroxyethyl)-am-*;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of May, A. D. 1951.

[SEAL]

**THOMAS F. MURPHY,**  
*Assistant Commissioner of Patents.*