This invention relates to the production of fibers, filaments, films and other shaped articles of regenerated cellulose. More specifically this invention is concerned with a viscose containing a modifying agent and the production of high tenacity, highly fatigue resistant fibers therefrom.

In the conventional method of producing regenerated cellulose articles from viscose, a suitable cellulose raw material such as wood pulp, cotton linters and the like is converted into alkali cellulose by steeping in a dilute caustic soda solution. The excess caustic soda is removed and the resultant alkali cellulose is shredded and then aged under carefully controlled conditions of temperature and humidity. The aged alkali cellulose is treated with carbon disulfide to form cellulose xanthate which readily dissolves in dilute caustic soda to produce viscose. The viscose solution is filtered, allowed to ripen and subsequently extruded through an orifice of the desired shape into a coagulating and regenerating bath to form the regenerated cellulose article.

In the production of filamentary articles such as filaments, fibers, yarns, tows, monofilaments, and the like, hereinafter referred to as fibers, the viscose solution is extruded through a spinneret of the desired number of hole openings and orifice size into a coagulating and regenerating bath consisting of an aqueous acid solution. The fiber while still in a partially regenerated state is stretched to improve its physical properties. Regeneration of the cellulose is then completed by treating the fiber with a dilute acid solution after which the residual acid and salts are removed by washing. Various additional treatments may also be accorded the fiber such as desulfurizing, bleaching and the like before it is dried and collected.

In the manufacture of high tenacity rayon fibers in recent years, numerous variations have been introduced in the process described above. The most significant innovation has been the incorporation of various additives or modifying agents in the viscose, the spin bath or both. Usually, it has been suggested that the modifier be present in the viscose. Among the many modifying agents that have been proposed, particular interest has been shown in polyalkylene glycols, ethoxylated fatty acids or esters, ethoxylated fatty alcohols, ethoxylated long chain aliphatic amines and the like. While the use of these additives has resulted in improved properties, their use has also created a number of problems in the maintenance of yarn quality under desirably economic conditions of spinning and processing. Generally, the presence of these modifying agents in the viscose has rendered the freshly extruded yarn more susceptible to damage in handling during the coagulation and early states of processing. In order to avoid substantial losses in yarn quality as a result of this, a number of process changes have been suggested such as the provision of means in the spin bath to protect the yarn, the maintenance of much closer controls over the composition of the bath and of the viscose, the reduction in the rates of spinning and processing used, and the like. Tubs or other baffling used in the spin bath to protect the weak partially coagulated individual filaments have proven to be difficult to operate particularly when the spinning is first started. Closer control of the composition of the bath and the viscose is difficult to achieve within close limits on a large scale production basis in the face of the huge volumes of liquids used and the normal fluctuations in plant production. Substantial reductions in the rates of spinning and processing is economically undesirable although this is the remedy generally resorted to.

It has been suggested that reduced rates of spinning can be avoided along with realizing other advantages by either heating the viscose just prior to extrusion or by maintaining the spin bath at a high temperature. The temperature at which spinning can be carried out is limited, however, because most of the modifying agents, particularly the polyalkylene oxide and ethoxylated types, exhibit decreasing solubility in caustic soda at these higher temperatures. This results in the modifying agent coming out of the solution, hence, reducing its effectiveness in achieving the improved properties desired.

It has also been found that while the tenacity of the yarn has been substantially increased by the use in the viscose of the polyalkylene oxide type modifying agents suggested in the art, the fatigue resistance of the yarn, particularly under heat, has not been increased to a proportional degree. In the use of high tenacity rayon in mechanical rubber goods such as in automobile veyor belts and the like, the fatigue resistance of the fiber under the conditions of heat developed by these articles in operation is particularly significant.

It has now been discovered that the incorporation in the viscose of a relatively small amount of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound having at least about four terminal hydroxyl units per nitrogen atom and mixtures of such derivatives permits the production of high tenacity fibers with improved continuity of spinning at higher temperatures. Modifiers of this type exhibit high turbidity points and low heteropoly acid precipitation factors, they require small concentrations and permitting viscose handling and spinning at higher temperatures without premature separation of the modifier from the viscose before extrusion. Furthermore, fibers produced in the practice of this invention display the desired high tenacity with improved resistance to fatigue at the elevated operating temperatures required by reinforced rubber goods.

In accordance with this invention, it has been found that an improved fiber forming viscose spinning solution can be produced by incorporating into the viscose a relatively small amount of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound having at least about four terminal hydroxyl units per nitrogen atom. In the process of this invention, a viscose spinning solution containing a relatively small amount of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound having at least about four terminal hydroxyl units per nitrogen atom is extruded into an aqueous sulfuric acid coagulating bath thereby producing a regenerated cellulose filamentary article having improved tenacity and fatigue resistance.

The nitrogen containing compounds which when suitably alkylated may be used in the modification of viscose in accordance with this invention include ammonia, alkyl amines, alkyl polycamines and alkyl amidines having alkyl substituents of no more than about 6 carbon atoms. These nitrogen containing compounds are alkylated with at least one mole per nitrogen atom of a diepoxide and sufficient additional diepoxides and/or epoxalkanes to produce polyalkylene oxide chains of from about 5 to about 120 alkylene oxide units. The alkylation with a diepoxide produces increased branching in the derivative which results in advantageously high turbidity points and low heteropoly acid precipitation factors as hereinafter described in more detail. The term "terminal hydroxyl group" as used herein means a hydroxyl group
which terminates a polyalkylene oxide chain or polyalkylene oxide branch chain.

In the practice of this invention, polyalkylene oxide derivatives of nitrogen containing compounds are used which have turbidity points above the temperature at which spinning is carried out. By the expression "turbidity point" it is meant, the temperature at which a 7.5% aqueous sodium hydroxide solution containing about 30% of the modifier just begins to become turbid indicating its incipient precipitation out of solution. The determination of turbidity point in clear aqueous caustic soda permits more accurate results than when carried out in viscose; the results, nevertheless, are equally valid as a measure of the precipitation point of the modifier out of the viscose solution. The importance of avoiding premature precipitation of the modifier from the viscose in the spinning of high tenacity, regenerated cellulose yarns is apparent not only from the fact that the modifier is not then able to effectively participate in the regulation and regeneration of the fiber but also because it may form globules of modifier about the spinning orifices and cause broken and reduced denier filaments in the yarn. Broken and reduced denier filaments are the most common causes of interruptions in the continuity of spinning and the consequent reduction in the quality of the yarn has resulted in the expenditure of considerable effort by the industry in the avoidance of these problems.

It has been found that as the number of branches of relatively short polyalkylene oxide chains having terminal hydroxyl groups are increased on the nitrogen containing compound the higher the turbidity of that compound. This can be seen by referring to the FIGURE wherein the turbidity point curves of a number of modifying agents suggested in the art are shown along with a modifier of this invention as the total number of ethylene oxide units per molecule are varied. Curve A represents the turbidity points of polyalkylene oxide derivatives of ammonia having four terminal hydroxyl groups in which the polyalkylene oxide chains contain one di- oxybutylene unit and the remainder are ethylene oxide units. Curve B represents the turbidity points of ethoxylated diamines such as Armour & Co.'s "Ethodiamine" which are comprised of ethylene diamine alkylated with tallow and ethoxylated to give a derivative with three terminal hydroxyl groups. Curve C represents the turbidity points of ethoxylated amine type modifiers such as Armour & Co.'s "Ethomeene" which consist of cocoammonium reacted with ethylene oxide and has two terminal hydroxyl groups. These curves graphically demonstrate the increase in turbidity points of representative nitrogen containing compounds with increases in branching and shows the advantageously higher turbidity points of the derivatives of those with at least four terminal hydroxyl groups.

In addition to the improved turbidity points of the polyalkylene oxide derivatives of the nitrogen containing compounds of this invention, the heteropoly acid precipitation factors of these compounds are much lower than those of the compounds suggested in the art. It has been proposed that effective viscose modifying agents should be easily precipitated in a viscose solution so as not to unduly interfere with the coagulation of the viscose gel, hence the suggested use of the highly insoluble monoamines. Although it is not intended to limit this invention by a theory, it is believed that the significance of the solubility in a viscose solution of these polyalkylene oxide derivatives is in their heteropoly acid precipitations. Heteropoly acid precipitation factors are determined by precipitating the modifier with a heteropoly acid such as silicotungstic acid, phosphotungstic acid, or a polynonylic acid as described in more detail by A. Barber, C. C. T. Chinnick, and P. A. Lincoln in The Analyst, volume 81, pages 18–25 (1956).

The significance of these factors lies in the presence in the viscose of the heteropoly acid, cellulose xanthic acid. The incipient precipitation of the cellulose xanthic acid promotes the uniform coagulation of the viscose gel and results in improved lower gel swell factors. Modifiers having increased branching with the resultant increase in available thermal hydroxyl groups exhibit advantageously lower heteropoly acid precipitation factors. As used herein, the heteropoly acid precipitation factors are expressed as the ratio of the moles of modifier to the moles of precipitated acid, in this case phosphotungstic, in the precipitate, hence, the smaller the ratio the greater the precipitating power of the modifier. Particular advantages have been found in the modifiers of this invention which have heteropoly acid precipitation factors below about 0.2.

In Table 1, below, are recorded the heteropoly acid precipitation factors for the following modifiers: (A) polyalkylene oxide derivative of ammonia having four terminal hydroxyl groups in which the alkylene oxide units total about 25 one of which is di oxybutylene and the remainder are ethylene oxide units; (B) ethoxylated sorbitol having a total of about 40 ethylene oxide units; (C) and ethylene oxide derivative of the glycerol ester of ricinoleic acid containing 80 moles of ethylene oxide marketed by Atlas Company under the trade designation "G-1298."

**TABLE 1**

<table>
<thead>
<tr>
<th>Modifier</th>
<th>Heteropoly acid precipitation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.172</td>
</tr>
<tr>
<td>B</td>
<td>0.204</td>
</tr>
<tr>
<td>C</td>
<td>0.274</td>
</tr>
</tbody>
</table>

The derivatives which may be used in the modification of the viscose in accordance with this invention are alkali soluble polyalkylene oxide derivatives of a nitrogen containing compound having at least about four terminal hydroxyl units per nitrogen atom. Although other nitrogen containing compounds may be used, greater advantages have been found in using a compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines and alkyl amides. Preferably, the alkyl groups should contain no more than about 6 carbon atoms. The polyalkylene oxide chains consist of alkylation of oxo units made up of the reaction products of epoxyalkanes and diepoxyalkanes containing at least about 2 carbon atoms and totaling between about 4 and about 120 moles. The derivative must contain at least one diepoxyalkane of the general formula:

\[
\text{R}_1\text{C}-(\text{CH}_2\text{O})_\text{K}\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-(\text{CHO})_\text{L}\text{N}^{-1}\text{N}\text{E}._\text{H}.
\]

wherein \(\text{R}_1\) and \(\text{R}_4\) represent hydrogen or alkyl groups having between 1 and 4 carbon atoms and \(\text{E}_\text{H}\) is an alkylene oxide unit having between 0 and 5 carbon atoms. The balance of the polyalkylene chains are made up of ethylene and/or propylene oxide units. The order and recurrence of the alkylene oxide units in the chain does not affect the utility of the derivative as long as it meets the limitation set out above and is alkali soluble having a turbidity point of at least about 45 and preferably at least about 60. Particular advantages have been found in using alkali soluble polyalkylene oxide derivatives of ammonia having at least four terminal hydroxyl groups and between about 4 and about 120 alkylene oxide units. In the preferred embodiment of this invention the modifier has the general formula:

\[
\text{H}_3\text{N}^{-1}\text{N}\text{E}._\text{H}.
\]

wherein \(x\) is at least two but no more than three and \(\text{K}, \text{L}, \text{M}\), and \(\text{N}\) are whole numbers whose sum is at least about 6 but no more than about 120. It should be noted
that the derivative does not necessarily have to include both ethylene and propylene oxide units but may advantageously be made up of only one and preferably ethylene oxide units.

The components useful in the practice of this invention may be prepared by reacting with the ammonia, alkyl amine, alkyl polyamine, or alkyl amide at least about one mole of an alkyl diepoxy and a sufficient number of additional moles of epoxyethylenes, propylene glycol, or mixtures of the two to produce the polyalkylene oxide chain length required. When any of the chains are terminated by an alkyl diepoxy unit, it is advantageous to hydrolyze the epoxy group to a hydroxyl group.

In instances where ammonia is used as the nitrogen containing starting material, it may be desirable to use the appropriate alkanolamine such as triethanolamine and thus increase the total number of alkylene oxide units by further reacting this product with the appropriate epoxy and/or diepoxy alkanes. The conditions under which alkylation may be carried out are well known in the art. For example, MacLaurin and Israel in U.S. Patent No. 2,593,466 describe in some detail the alkylation of long chain aliphatic amines. Lusted in U.S. Patent No. 2,674,619 describes the preparation of polyalkylene chains of increased length, and Clark and Winslow in U.S. Patent No. 2,897,163 describe the production of polymeric materials from alkylene oxides and butadiene diepoxy.

It has been found that an improved viscose spinning solution results when the modifiers of this invention are utilized in a viscose comprised of between about 5% and about 9% cellulose, between about 4% and about 8% caustic soda and a total sulfur content of between about 25% and about 55% based on the weight of the cellulose. Total sulfur contents within this range may be achieved by the addition of between about 30% and about 60% carbon disulfide on the weight of the cellulose either in a one step process to the aged alkali cellulose or in a two step process wherein about 80% is added to the aged alkali cellulose crumbs and the balance after partial dissolving of the crumbs. At the time of extrusion, the modified viscose should preferably have an index of at least about 4.5 and a viscosity between about 30 and about 200 bbl fall seconds. The term "bbl fall seconds" as used herein is defined as the time in seconds for a 1.3 inch diameter ball having a density of 0.76 grams per cubic centimeter to fall 8 inches through the viscose solution.

Advantageously, it has been found that only relatively small amounts of these nitrogen containing derivatives are necessary to obtain the improved results herein described. Substantial reductions in the amount of modifier necessary over the amounts suggested in the art can be achieved with these derivatives while still obtaining comparable products. Generally, it is advantageous to use between about 0.2% and about 5% of the polyalkylene oxide derivatives of this invention based on the weight of the cellulose in the viscose and particular advantages result from using from about 0.25% to about 2% on the weight of the cellulose of these derivatives. The concentration of the modifier in the viscose refers to the concentration at the time of extrusion and the amount which must be added to achieve this result may vary somewhat since the derivative may be introduced at any stage in the viscose process after the steeping of the wood pulp. It has been found that when the derivative is added to the pulp a substantial amount is lost in the steeping liquors due to its advantageous solubility in caustic soda. Any means of obtaining the concentration of modifier mentioned above at the time of extrusion, therefore, is contemplated by this invention although preferably the derivative is added during dissolving of the xanthate and prior to the filtration of the resulting viscose solution.

The coagulating bath used in conjunction with the viscose described including the modifier consists of an aqueous solution of sulfuric acid, sodium sulfate, and a soluble heavy metal sulfate, such as zinc sulfate, whose concentrations have been adjusted with relation to the concentration of the components of the viscose. Advantageously, the use of the modifiers of this invention permits a greater flexibility in the range of these adjustments than has heretofore been achievable in high tenacity fiber production employing modifiers, this flexibility is achieved without sacrifice of the practical continuity of spinning.

Of particular concern in these adjustments is the sulfuric acid content of the bath. In general, the practical lower limit of the acid concentration is determined by the concentration at which slubbing begins to occur. By "slubbing" is meant the formation on the spinneret face of small globules of uncogulated viscose which appear as the filaments as they emerge from the bath as thick particles enmeshed in the yarn. This occurs when the acid concentration is too low to cogulate the viscose as it emerges from the spinneret orifices and, in practice, is avoided by maintaining the acid concentration at about 0.5% above the concentration at which slubbing can be visually detected. The upper limit of acid concentration depends upon the rate of diffusion of the acid into the viscose gel structure which, when it is too high, results in a yarn of low tenacity and poor fatigue characteristics.

Generally, the acid concentration may be about 10% by weight to avoid this and particular advantages have been found in maintaining the concentration of sulfuric acid between about 4% and about 9.5%.

As to the concentration of sodium sulfate and zinc sulfate in the coagulating bath, it has been found particularly advantageous to maintain the sodium sulfate between about 6% and about 25% and the zinc sulfate between about 3% and about 15% with a preferred range of concentration of sodium sulfate between about 8% and 21%.

Advantageously, the incorporation of the polyalkylene oxide derivative in the viscose results in its appearance in the bath where it acts as an incrustation and cramping inhibitor and, thus may eliminate or reduce the amount of other organic bath additives suggested in the art to prevent the formation of these deposits. As mentioned above, one means suggested for improving the continuity of spinning modified viscose yarns is the heating of the spin bath. By reason of their high turbidity points these modifiers permit a much greater range of bath temperatures which generally vary between about 30° C. and 95° C. or higher. Greater advantages have been found, however, in maintaining the temperature of the spin bath between about 45° C. and about 80° C. and preferably the spin bath is controlled between about 55° C. and about 75° C.

This invention now will be more fully described by the following examples, although it is understood that the invention is not to be limited thereby. In these examples, "parts" and "percent" of materials are intended to mean parts and percent by weight.

Example I

A viscose solution is prepared in the following manner. Sheets of rayon grade wood pulp containing about 96.8% alpha cellulose are steeped in a 19% sodium hydroxide solution for 60 minutes at 24° C. The excess caustic soda is then pressed from the resulting alkali cellulose to give a press weight ratio of 2.8:1. The alkali cellulose is then treated in a continuous shredding device at a temperature of 28.5° C. The shredded alkali cellulose is then aged at 28° C. for a period adjusted to give a viscose viscosity of about 100 bbl fall seconds. After aging, the alkali cellulose is charged into a barrette and 46% carbon disulfide based on the weight of the cellulose is introduced. The barrette is revolved thoroughly mix the alkali cellulose and carbon disulfide and thus facilitate the formation of the xanthate while the temperature is maintained below about 33° C.

The cellulose xanthate is then charged into a mixer tank containing an aqueous caustic soda solution in an
amount adjusted so that the viscose formed will have a 6.5% cellulose, 7.0% caustic content. The solution is mixed for 2½ hrs, during which there is added 1.25% based on the weight of the cellulose of an alkylene oxide derivative of ammonia having the formula:

\[
\text{H} \quad \text{H} \quad \text{H} \\
\text{C}(\text{CH}_2\text{O})_n\text{H} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \\
\text{N} \quad \text{H} \quad \text{H} \\
\text{H} \\
\text{C}(\text{CH}_2\text{O})_m\text{H}
\]

where \( x \) is two and the ethylene oxide units total 25. The viscose is filtered, desalted and ripened to a salt index of 8.3.

The viscose is extruded through a spinneret into a spin bath containing 6.0% sulfuric acid, 13% sodium sulfate, 7.2% zinc sulfate maintained at about 65° C. to form an 1100 denier, 720 filament yarn. Upon withdrawal of the yarn from the spin bath it is stretched about 90% between two yarn-storing, yarn-advancing devices of the type described in U.S. Patent No. 2,210,914 while a 90° C. water solution is applied to the yarn as it is stretched. The yarn is then continuously processed over a series of yarn-storing, yarn-advancing reels upon which various treatments are carried out including the application of a dilute acid bath to complete regeneration, the washing-out of the salts and acids deposited on the yarn, the lubrication of the yarn and drying. Finally, the yarn is collected at about 30 meters per minute on a bobbin.

Properties of the yarn and a 2-ply, 14 x 14 twist cord resulting therefrom are recorded in column A of Table 2 below. For comparison, properties of several high tenacity yarns of the prior art are given in columns B and C of Table 2. Yarn B is produced using 2.0% of Armon & Company's "Etheneen C-40" which is comprised of ethylene oxide alkylated with tallow and ethoxylated with 30 moles of ethylene oxide as a modifier. Yarn C is a control yarn produced without a modifier.

### Table 2

<table>
<thead>
<tr>
<th>Yarn Cond. Tenacity (g./d.)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yarn Wet Tenacity (g./d.)</td>
<td>5.6</td>
<td>5.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Cord Fatigue Fatigue (lbs.)</td>
<td>100</td>
<td>155</td>
<td>100</td>
</tr>
</tbody>
</table>

In predicting the performance of a yarn when it is used as a reinforcing material for mechanical rubber goods by its properties prior to its use, it is desirable to approximate the conditions of operation as closely as possible. Due to the constant flexure of cord reinforced rubber articles, considerable heat is developed in the article. Flexure fatigue of the yarn under these hot conditions is one of the primary sources of failure of cord made from high tenacity yarns, and hence, a significant basis for yarn and cord comparison. The heat fatigue results shown in Table 1 were obtained from a vibration fatigue test wherein a pair of 1100 denier yarns twisted into a 14 x 14 cord is rotated at a rate of 3000 cycles per minute. The time in hours required to cause failure of the cord is recorded and converted into the heat fatigue index by dividing it by the time required to cause failure of the unmodified cord and multiplying by 100. The results indicate that although the tenacies of the yarns are comparable, the heat fatigue of yarn produced using the polyalkylene oxide derivative of ammonia in accordance with this invention is distinctly superior.

### Example II

A viscose is prepared as described in Example I but with a cellulose and caustic soda content of 6.3% and 7.6% respectively and with 1% of a modifier consisting of a polyalkylene oxide derivative of ammonia having mixed chains resulting from the reaction of ammonia with a mixture of epoxyethylen and diepoxide butadiene. The polyalkylene oxide chains total 30 alkylene oxide units, 1% of which are dioxybutylene and the balance of which are ethylene oxide. The viscose is filtered, desalted, and ripened to a salt index of 5.8.

The viscose is extruded through a 720 hole spinneret into a spin bath containing 6.2% sulfuric acid, 8.9% zinc sulfate, and 12% sodium sulfate maintained at 60° C. to form an 1100 denier yarn. The yarn, while about 75% regenerated, is stretched about 92% while in contact with 95° C. water after which regeneration is completed, the acid and salts washed out of the yarn, and the yarn dried and collected at about 30 meters per minute. Spinning of these fibers proceeds continuously and results in a yarn having few slubs, knots, or other imperfections appearing in off-quality yarn. The resultant individual filaments have a smooth non-crimped, non-wrinkled surface and a cross-section consisting substantially entirely of skin.

Other properties of the yarn are shown in Table 3, below, wherein more specific comparison of the yarn with unmodified yarn can be made.

### Example III

A viscose is prepared as described in Example I with a 1.5% of an alkylene oxide derivative of dimethyl amine with alkylene oxide chains consisting of 3 dioxybutylene units and 6 ethylene oxide units. The viscose is ripened to a salt index of about 6 and is extruded through a spinneret to form an 1100 denier, 720 filament yarn. The spin bath into which the viscose is spun contains 6.7% sulfuric acid, 12% sodium sulfate, 8.5% zinc sulfate and is maintained at about 65° C. The yarn is stretched about 90% while a stream of 95° C. is sprayed over it. Subsequently, regeneration is completed, the acids and salts washed out, the yarn dried and collected at about 27 meters per minute.

The physical properties of the resulting yarn are recorded below in Table 3. In contrast to the control yarn this modified yarn has distinctly improved properties of tenacity and exhibits filmation cross-sections which are uniformly all-skin.

### Example IV

Approximately 1% of an alkylene oxide derivative of acetamide is added to a viscose preared as described in Example I. The modifier in this case has alkylene oxide chains consisting of 2 dioxybutylene units and 100 ethylene oxide units. The viscose is ripened to an index of about 7.0 and extruded through a 720 filament hole spinneret to form an 1100 denier yarn. The spin bath into which the viscose is extruded contains 6.7% sulfuric acid, 12% sodium sulfate, 8.5% zinc sulfate and is controlled at about 66° C. Upon emergence from the coagulating bath the yarn is stretched in a secondary bath of hot water about 95%. The yarn is then regenerated in a dilute acid solution, washed, oiled, dried, and collected at about 30 meters per minute.

The tenacity of the yarn as shown in Table 3, below, is substantially greater than that of the control yarn and its continuity of spinning is improved over the spinning of yarns wherein modifiers of the type described earlier are used. Also, yarn produced in accordance with this example exhibit superior heat fatigue resistance on the order of that demonstrated in Table 3.
It is known that filaments having smooth surfaces with no appreciable crenulation have outstanding resistance to soiling, fibrillation and, of particular interest, improved resistance to fatigue. Also, it is known that fiber cross-sections consisting substantially entirely of skin exhibit greatly improved tenacity and flexing life over filaments produced according to prior art methods. As can be seen from Table 3 above, the fibers produced in accordance with this invention are substantially non-crenulated to the point that when the optimum balance between the bath and viscos composition is attained the cross-sectional periphery is smooth and substantially round. Also, the cross-sections of the fibers of this invention are substantially all-skin and as such result in an improved conversion of yarn strength into cord strengths. That is, when conventional yarns are twisted into cord as in the production of tire cord there may result an appreciable loss in tensile strength. All-skin yarns, however, lose appreciably less tensile strength when converted to cord and are, therefore, particularly desirable for use in high tenacity applications.

It is also known that the general strength, fatigue resistance and quality of viscos yarns are improved by the reduction of the primary swelling of the gel fibers. In the art, this is known as the “gel swelling factor” of the fiber and may be determined with equal validity in either the fiber or film form of the viscos. When it is determined in the film, the particular viscos to be tested is spread on a glass plate in a film of 0.010 inch thickness. This film is immersed for 30 seconds in a spin bath whose composition has been adjusted in accordance with the cellulose and caustic content of the viscos. The film is then blotted dry and weighed to give the “blot film weight.” This film is then dried at 110°C. for two hours and again weighed to give the “dry film weight.” The gel swelling factor is then determined in accordance with the following equation.

\[ \text{Gel swell factor} = \frac{\text{blot film weight}}{\text{dry film weight}} \]

For purposes of convenience the gel swelling factors are divided by the gel swelling factors of an unmodified control viscos to give the gel swelling factor ratio (G.S.F. ratio). In Table 4, below, the G.S.F. ratios of a number of modified viscoses in comparison with the unmodified viscos of Example I(c) are recorded. Viscose A is the viscos prepared as described in Example I with a concentration of 0.5% on the weight of the viscos of the ammonia derivative therein described. Viscose B is a viscos prepared as described in Example I but with the ammonia derivative replaced with 0.5% on the weight of the viscos of the ethoxylated glycerol ester of ricinoleic acid containing 80 moles of ethylene oxide. Viscose C is a viscos prepared as described in Example I but with 0.5% on the weight of the viscos of ethoxylated sorbitol containing 100 moles of ethylene oxide such as that marketed by Atlas Company under the designation “G-2010” substituted as a modifier. Viscose D represents a viscos as described in Example I but having substituted for the modifier 0.5% on the weight of the viscos of the ethoxylated amine described above in the discussion of heteropoly acid precipitation factors.

<table>
<thead>
<tr>
<th>Viscose</th>
<th>G.S.F. Ratio</th>
<th>Neutralization Time Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.80</td>
<td>1.2</td>
</tr>
<tr>
<td>B</td>
<td>0.85</td>
<td>2.85</td>
</tr>
<tr>
<td>C</td>
<td>0.75</td>
<td>3.3</td>
</tr>
</tbody>
</table>

The gel swell ratio of viscos containing the modifiers of this invention are significantly lower than those of viscoses containing the known additives in the art at the same concentrations of additive. These results are due primarily to the advantageously high turbidity points of this modifier which indicate the ready availability of this modifier in the viscos. The combination of high turbidity point and low gel swell factor ratio has practical application in the production of fibers and the economics of high tenacity yarns from modified viscos in permitting the spinning of such viscoses at higher temperatures and, hence, with better continuity while obtaining high tenacities and improved fatigue resistances.

Another important indication of yarn quality attainable from a particular viscos is the “neutralization time” recorded in Table 4 above. This factor refers to the time of neutralization of the viscos within the spin bath. It is determined as described in U.S. Patent No. 2,356,014 and for purposes of comparison has been converted here to a ratio on the basis of the unmodified viscos. It has been found that viscoses which exhibit an increase in their neutralization time over those of the prior art result in yarn and cords of improved properties. An increase in the neutralization time indicates that greater delay of the viscos before permanent set of the gel structure of the fiber is caused by the inclusion of the modifier. In this case, with the gel swell data, it can be seen that advantageously improved neutralization times are obtained using the instant modifiers and that fibers produced by this process would, therefore, have characteristically improved tenacity and fatigue properties.

In the process of this invention the alkali cellulose is prepared in the conventional manner. Sheets of cellulose such as wood pulp, cotton linters or a mixture of the two may be used depending upon, among other things, the characteristics desired in the ultimate products. Wood pulp found particularly desirable contains at least about 95% alpha cellulose with no more than about 0.5% of residual natural ether extractable resins. The cellulose sheets are first soaked in aqueous sodium hydroxide solution; the excess caustic solution is drained and pressed from the sheets and the resulting alkali cellulose is shredded and aged. The shredded alkali cellulose crumbs are then dropped into a mixing drum where they are xanthated.

Xanthation is carried out by tumbling the alkali cellulose crumbs with about 30% and about 60% carbon disulfide in the weight of the carbon disulfide in this range of concentrations results in a total sulfur content of about 25% and about 55% based on the weight of the cellulose. The xanthated alkali cellulose is then introduced into a mixing tank or dissolver where it is mixed with the proper amount of dilute aqueous caustic soda solution to produce a final viscose solution consisting of about 5% and about 9% cellulose and between 4% and about 8% caustic soda. The ammonia derivative modifier is preferably added during the mixing cycle but it may be introduced by adding it to any of the materials used in producing the viscos. The modifier may also be introduced directly into the viscose stream by injection, for example. The good solubility of these modifiers results in rapid and thorough mixing permitting introduction just prior to extrusion. The injection of the modifier at this late stage in the preparation of the viscose advantageously reduces possible losses which might be incurred during the treatments accorded the viscose after dissolving.

The viscose solution is then filtered, deaerated, and ripened before being extruded into fibers at a gamma number, as defined in U.S. Patent No. 2,703,270, at the extrusion nozzle of between about 35 and about 85. It has been proposed in the art that the viscos be heated prior to extrusion and several methods of accomplishing this have been suggested, such as, placing a small heat exchanger in the line, coiling the tube to the spinneret and submerging it in a hot bath and the like. Ordinarily, however, the extrusion nozzle or spinneret is submerged in the spin bath sufficiently to result in substantially rais-
ing the temperature of the viscose before it is extruded. The use of higher temperature spin baths has contributed to this so that for the purposes of this invention no unusual provisions need be made for heating the viscose spinning solution.

The viscose spinning solution is extruded through a spinneret into a coagulating and regenerating bath adjusted in accordance with the concentration of cellulose and caustic therein and containing sulfuric acid, sodium sulfate, and a soluble heavy metal sulfate, preferably zinc sulfate. Part of the zinc sulfate may be replaced by any of a number of other metal sulfates taught in the art, such as sulfates of iron, manganese, cobalt, nickel, cadmium and the like. Also, included in the bath may be small amounts of organic bath additive suggested in the art to prevent the formation of spinneret incrustations. Advantageously, the alkylene oxide derivatives of this invention which wash out of the freshly extruded fibers into the bath also act as incrustation inhibitors. By the proper control of the accumulation of the modifier in the bath, the use of other bath additives may advantageously be reduced or eliminated. The temperature of the spin bath may be maintained at between about 30°C and about 35°C in order to facilitate coagulation and aid in maintaining spinning by-products in solution.

In order to obtain optimum tenacities in viscose yarn it is necessary to stretch the yarn prior to its achieving complete regeneration. This may be carried out immediately after the removal of the yarn from the spin bath while it is still about 75% regenerated. During the stretching, filaments may be immersed in a hot aqueous secondary bath or a hot aqueous liquid applied to them. The secondary bath may consist simply of water or dilute (1 to 5%) acid or dilute coagulating bath at a temperature between about 75°C and about 125°C. The stretching time may be effected in one or more steps and amounts to an increase in length of about 70% to 170% depending upon the properties desired and the degree of stretching the partially regenerated yarn will withstand. Yarns which are used for textile purposes and, hence, do not require high tenacities may be stretched to a much smaller degree while still obtaining the improved properties of abrasion and fatigue resistance.

After stretching, the regeneration of the yarn is completed by applying a hot aqueous solution usually containing about 2% sulfuric acid and relatively small amounts of sodium sulfate and zinc sulfate. In the completely regenerating form, the yarn may then be subjected to a series of finishing treatments including washing, drying, slashing and the like. These treatments may be carried out either in a discontinuous manner as when the yarn is produced by the conventional bucket or spool spinning process or they may be carried out using the continuous process, thus avoiding the necessity of multiple yarn transfers of the yarn packages to the treating solutions.

The improved yarns produced by the practice of this invention find particular utility in cords and fabrics for the reinforcement of automobile and truck tires. The high tenacity and high heat fatigue of these yarns and cords substantially prolongs the useful life of the rubber products in which they are used. These cords are also useful in reinforcing rubber power transmission belts, so called V-belts, and conveyor belts. Textile yarns made in accordance with this invention also exhibit enhanced properties such as abrasion resistance, higher strength, ease of finishing and the like.

Since certain changes in the practice of this invention may be readily made without substantially departing from its spirit or scope, it is to be understood that all the foregoing be interpreted as being merely illustrative and is not to be construed as limiting or restricting the invention as particularly pointed out and defined in the appended claims.

What is claimed is:

1. A fiber forming viscose spinning solution containing from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines, and alkyl amides said derivative having polyalkylene oxide chains of from about 5 to about 120 alkylene oxide units and at least about four terminal hydroxyl units per nitrogen atom.

2. A viscose spinning solution comprising about 5% to about 9% cellulose, about 4% to about 8% sodium hydroxide, and about 25% to about 55% total sulfur based on the weight of the cellulose having incorporated therein from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines, and alkyl amides said derivative having polyalkylene oxide chains comprised of between about 5 and 120 alkylene oxide units selected from the group consisting of ethylene oxide, propylene oxide, and mixtures of ethylene oxide and propylene oxide, and at least about one mole per nitrogen atom of the reaction product of a dienepolyalkylene oxide containing of the general formula:

\[
\text{H}_2\text{C}_n=\text{O}-\text{CH}_2\text{O}\left(\text{CH}_2\text{O}\right)_m\text{H}
\]

wherein R1 and R2 represent members selected from the group consisting of hydrogen and alkyl groups having between 1 and 4 carbon atoms and R3 represents an alkylene radical having between 0 and 5 carbon atoms and said derivative having at least about four terminal hydroxyl units per nitrogen atom.

3. A viscose spinning solution for the production of high tenacity, highly fatigue resistant regenerated cellulose filamentary articles containing from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of ammonia having the general formula:

\[
\text{H}_2\text{C}_n=\text{O}-\text{CH}_2\text{O}\left(\text{CH}_2\text{O}\right)_m\text{H}
\]

wherein \(x\) is at least two but no more than three and \(K\), \(L\), \(M\), and \(N\) are whole numbers whose sum is at least about 6 but no more than about 120, said derivative having a turbidity point of at least about 45.

4. A viscose spinning solution for the production of high tenacity, highly fatigue resistant filamentary articles comprising about 5% to about 9% cellulose, about 4% to about 8% sodium hydroxide, and about 25% to about 55% total sulfur based on the weight of the cellulose having incorporated therein from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble product formed by the hydrolysis of the reaction product of a nitrogen containing compound selected from the group consisting of amino compounds, alkyl amines, alkyl polyamines, and alkyl amides with at least about one mole per nitrogen atom of an alkyl diepoxide and sufficient additional moles of an epoxyalkane selected from the group consisting of epoxystyrene, epoxypropylene, and mixtures of epoxyalkane and epoxypropylene to produce polyalkylene oxide chains totaling between about 6 and about 120 alkylene oxide units per mole of said nitrogen containing compound, said hydrolyzed reaction product having at least about four terminal hydroxyl units per nitrogen atom.

5. In a process for the production of regenerated cellulose shaped articles of substantially improved tenacity and fatigue resistance the step comprising, extruding into an
aqueous sulfuric acid coagulating bath a viscose spinning solution containing from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines, and alkyl amides said derivative having polyalkylene oxide chains of from about 5 to about 120 alkylene oxide units and at least about four terminal hydroxyl units per nitrogen atom.

6. In a process for the production of regenerated cellulose filamentary articles of substantially improved tenacity and fatigue resistance the step comprising, extruding into an aqueous sulfuric acid coagulating bath at about 45°C a viscose spinning solution containing about 5% to about 9% cellulose, about 4% to about 8% sodium hydroxide, about 25% to about 55% total sulfur based on the weight of the cellulose, and from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines, and alkyl amides said derivative having polyalkylene oxide chains of from about 5 to about 120 alkylene oxide units and at least about four terminal hydroxyl units per nitrogen atom and a turbidity point above the temperature employed in spinning.

7. An improved process for spinning regenerated cellulose filamentary articles of substantially improved tenacity and fatigue resistance comprising, extruding into an aqueous coagulating bath a viscose containing about 5% to about 9% cellulose, about 4% to about 8% sodium hydroxide, about 25% to about 55% total sulfur based on the weight of the cellulose and from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of a nitrogen containing compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines, and alkyl amides said derivative having polyalkylene oxide chains of from about 5 to about 120 alkylene oxide units and at least about four terminal hydroxyl units per nitrogen atom and a turbidity point of at least about 45; said aqueous coagulating bath comprising about 4% to about 10% sulfuric acid, about 6% to about 25% sodium sulfate, and about 3% to about 15% zinc sulfate.

8. In a process for the production of regenerated cellulose yarn of substantially improved tenacity and fatigue resistance the step comprising, extruding into an aqueous sulfuric acid coagulating bath a viscose spinning solution containing about 5% to about 9% cellulose, about 4% to about 8% sodium hydroxide, about 25% to about 55% total sulfur based on the weight of the cellulose and from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble polyalkylene oxide derivative of ammonia having the general formula:

\[
\begin{align*}
(C_2H_5O)xH & \quad \text{wherein } x \text{ is at least two but no more than three and } K, L, M, \text{ and } N \text{ are whole numbers whose sum is at least about 6 but no more than about 120, said derivative having a turbidity point of at least about 45.}
\end{align*}
\]

9. In a process for the production of regenerated cellulose yarn of substantially improved tenacity and fatigue resistance the step comprising, extruding into an aqueous sulfuric acid coagulating bath a viscose spinning solution containing about 5% to about 9% cellulose, about 4% to about 8% sodium hydroxide, about 25% to about 55% total sulfur based on the weight of the cellulose and from about 0.2% to about 5%, based on the weight of the cellulose, of an alkali soluble product formed by the hydrolysis of the reaction product of a nitrogen containing compound selected from the group consisting of ammonia, alkyl amines, alkyl polyamines, and alkyl amides with one mole per nitrogen atom of an alkyl di-epoxide and sufficient additional moles of an epoxide alkane selected from the group consisting of epoxycyclohexane, epoxycyclopentane, and mixtures of epoxycyclohexane and epoxycyclopentane to produce polyalkylene oxide chains totalling between about 6 and about 120 alkylene oxide units per mole of said nitrogen containing compound, said hydrolyzed reaction product having at least about four terminal hydroxyl units per nitrogen unit.

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