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PROCESS OF PRODUCING VISCOSE RAYON

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4 Claims. (Cl. 106—165)

This invention relates to the production of shaped bodies of regenerated cellulose from viscose and more particularly to filaments and fibers of regenerated cellulose from viscose.

In the conventional methods of producing shaped bodies of regenerated cellulose from viscose, a suitable cellulosic material such as purified cotton linters, wood pulp, mixtures thereof, and the like is first converted to an alkali cellulose by treatment with a caustic soda solution and after shredding the threated cellulose material, it is allowed to age. The aged alkali cellulose is then converted to a xanthate by treatment with carbon disulfide. The cellulose xanthate is subsequently dissolved in a caustic soda solution in an amount calculated to provide a viscose of the desired cellulose and alkali content. After filtration, the viscose solution is allowed to ripen and is subsequently extruded through a shaped orifice into a suitable coagulating and regenerating bath.

In the production of shaped bodies such as filaments, the viscose solution is extruded through a spinneret into a coagulating and regenerating bath consisting of an aqueous acid solution containing zinc sulfate. The filament may subsequently be passed through a hot aqueous bath where it is stretched to improve its properties such as tensile strength. The filament may then be passed through a dilute aqueous solution of sulfuric acid and sodium sulfate to complete the regeneration of the cellulose, in case it is not completely regenerated upon leaving the stretching stage. The filament is subsequently subjected to washing, purification, bleaching, possibly other treating operations and drying, being collected either before or after these treatments.

The filaments as formed by the coventional methods, consist of a skin or outer shell portion and a core portion with a sharp line of demarkation between the two. The cross-section of the filaments exhibits a very irregular or crenulated exterior surface when even small amunts of zinc salts or certain other polyvalent metal salts are present in the spinning bath. The skin and core portions of the filament represent differences in structure and these different portions possess different swelling and staining characteristics, the latter permitting a ready identification of skin and core. The sharply irregular and crenulated surface structure has a relatively low abrasion resistance and readily picks up foreign particles such as dirt. Although the core portion possesses a relatively high tensile strength, it has a low abrasion resistance and a low flex-life, is subject to fibrillation and is relatively stiff.

It has now been discovered that the presence of small amounts of alkali-soluble alkylene oxide adducts of higher primary aliphatic alcohols in viscose results in the production of shaped bodies of regenerated cellulose such as filaments, films, sheets and the like composed of all skin and having improved properties and characteristics providing that the amount of the adduct is maintained with certain limits and the composition of the spinning bath is maintained within certain composition limits which will

be defined hereinafter. The most readily distinguishable characteristics as compared to conventional filaments include a smooth, non-crenulated surface and the filaments consist entirely of skin.

This invention contemplates the use of such compounds as are more technically classed as polyoxyalkylene glycol ethers of higher primary aliphatic or fatty alcohols such as, for example, the ethers of ethylene and propylene glycols and the alcohols. It is obvious that for all practical purposes considering cost, ease of preparation, commercial availability and solubility in water and alkali solutions such as a 6% caustic solution, the polyoxyethylene glycol derivatives are preferred. Accordingly, the invention will be illustrated by reference to polyoxyethylene glycol ethers. As is well known, the substances as commercially prepared generally are not pure compounds but consist of a group of ethers.

The higher primary aliphatic alcohols contemplated for use in the ethers contain from 8 to 24 carbon atoms, preferably from 12 to 18 carbon atoms. The ethers may be prepared from a relatively pure alcohol within the range or they may be prepared from technical grades of the alcohols or a mixture of the alcohols as derived from the acid radicals of naturally occurring fats and oils such as cottonseed oil, coconut oil, corn oil, soya bean oil, palm oils, peanut oil and the like and the hydrogenated fats and oils, the hydrocarbon chains being of the same number of carbon atoms as the fatty acids in which they have their origin. The alcohols derived from coconut oil, for example, will consist of a mixture of alcohols having from 8 to 18 carbon atoms with the individual alcohols in a distribution corresponding to the percentage distribution of the fatty acids of the particular coconut oil.

The polyoxyalkylene or polyoxyethylene content of the adducts or ethers may vary from about 20 to 200 and more alkylene oxide units per molecule of aliphatic alcohol, the preferred ethers containing from about 30 to about 150 ethylene oxide units per molecule. The ethers may be uniform in respect to the ethylene oxide chain or the substance may consist of a mixture of ethers having ethylene oxide chains of different length depending upon the method of preparation of the ethers. It is to be understood that for the purposes of this invention each of the chains of ethylene oxide units need not be identical.

The production of all skin products requires that certain minimum amounts of the ether be in solution in the viscose. Therefore, the minimum number of units of an alkylene oxide such as ethylene oxide required in the ether is that amount which imparts to the aliphatic alcohol ether sufficient alkali solubility whereby the minimum amount of ether can be dissolved in the viscose. The ether may be conveniently added to the viscose in the form of a solution in alkali or water. It is preferred to employ ethers having an alkylene oxide content in excess of the minimum requirement whereby the ether may be readily dissolved in and distributed uniformly throughout the viscose during the usual mixing stage employed in the production of the viscose.

The amount of the polyoxyalkylene glycol-aliphatic alcohol ether which is incorporated in viscose must be at least about 1% by weight of the cellulose in the viscose and may vary up to about 6%, preferably, the amount varies from 2% to 5%. Lesser amounts do not result in the production of products consisting entirely of skin and greater amounts affect adversely the physical properties of the products. Amounts within the preferred range are most effective in enhancing the characteristics and properties of the products. The polyoxyalkylene glycol-alcohol ether may be added at any one of the stages in the production of the viscose such as in the preparation

of the refined wood pulp for the manufacture of viscose, before or during the shredding of the alkali cellulose, to the xanthated cellulose while it is being dissolved in the caustic solution or to the viscose solution before or after filtration. The polyoxyalkylene glycol-aliphatic alcohol ether is preferably added after the cellulose xanthate has been dissolved in the caustic solution and prior to filtration.

The viscose may contain from about 4% to about 8% cellulose, the particular source of the cellulose being selected for the ultimate use of the regenerated cellulose product. The caustic soda content may be from about 4% to about 8% and the carbon disulfide content may be from about 30% to about 50% based upon the weight of the cellulose. The modified viscose, that is, a viscose containing the small amount of ether or modifier, may have a salt test above about 6 and preferably about 8 or higher at the time of spinning or extrusion.

In order to obtain the improvements enumerated hereinbefore, it is essential that the composition of the spinning bath be maintained within a well defined range. The presence of the polyoxyalkylene glycol-aliphatic alcohol ether in the viscose combined with these limited spinning baths results in the production of yarns of improved properties such as high tenacity, high abrasion resistance, high fatigue resistance and consisting of filaments composed entirely of skin.

Generically and in terms of the industrial art, the spinning bath is a low acid-high zinc spinning bath. The bath should contain from about 10% to about 25% sodium sulfate and from about 3% to about 15% zinc sulfate, preferably from 15% to 22% sodium sulfate and from 4% to 9% zinc sulfate. Other metal sulfates such as iron, manganese, nickel and the like may be present and may replace some of the zinc sulfate. The temperature of the spinning bath may vary from about 25° C. to about 80° C., preferably between about 45° C. to about 70° C. In the production of the all skin type filaments, the temperature of the spinning bath is not critical, however, as is well known in the conventional practice in the art, certain of the physical properties such as tensile strength vary directly with the temperature of the spinning bath. Thus, in the production of filaments for tire cord purposes in accordance with the method of this invention, the spinning bath is preferably maintained at a temperature between about 55° C. and 65° C. so as to obtain the desired high tensile strength.

The acid content of the spinning bath is balanced against the composition of the viscose. The lower limit of the acid concentration, as is well known in the art, is just above the slubbing point, that is, the concentration at which small slubs of uncoagulated viscose appear in the strand as it leaves the spinning bath. For commercial operations, the acid concentration is generally maintained about 0.4% to 0.5% above the slubbing point. For any specific viscose composition, the acid concentration of the spinning bath must be maintained above the slubbing point and below the concentration at which the neutralization of the caustic of the viscose is sufficiently rapid to form a filament having a skin and core.

There is a maximum acid concentration for any specific viscose composition beyond which the neutralization is sufficiently rapid to produce filaments having a skin and core. For example, in general, the acid concentration of the spinning baths which are satisfactory for the commercial production of the all skin products from a 7% cellulose, 6% caustic viscose and containing the polyoxyethylene glycol-aliphatic alcohol ethers lies between about 5% and about 8%. The acid concentration may be increased as the amount of modifier is increased and also as the salt test of the viscose is increased. There is an upper limit, however, for the acid concentration based upon the amount of modifier and the concentration of caustic in the viscose. All skin products cannot be obtained if the acid content of the bath is increased above the maximum value although the amount of the ether or modifier is increased beyond about 6% while other conditions are maintained constant. Increasing the caustic content of the viscose beyond about 8% is uneconomical for commercial production methods. For example, a viscose containing about 7% cellulose, about 6% caustic soda, about 41%, based on the weight of the cellulose, carbon disulfide and 3%, based on the weight of the cellulose, of a polyoxyethylene glycol ether of decanol having about 30 ethylene oxide units per molecule and the viscose having a salt test of 9 to 10 when extruded into spinning baths containing 16 to 20% sodium sulfate, 4 to 8% zinc sulfate and sulfuric acid not more than about 8%, results in the production of all skin filaments. Lesser amounts of sulfuric acid may be employed. Greater amounts of acid result in the production of products having skin and core. A lowering of the amount of modifier, the lowering of the caustic soda content or the lowering of the salt test of the viscose reduces the maximum permissible acid concentration for the production of all skin filaments. In any event, it has been determined that the maximum acid concentration which is permissible for the production of all skin products is about 8%.

The presence of the polyoxyalkylene glycol-aliphatic alcohol ethers in the viscose retards the coagulation and, therefore, the amount of the ether employed must be reduced at high spinning speeds. Thus, for optimum physical characteristics of an all skin yarn formed from a viscose as above and at a spinning speed of about 50 meters per minute, the ether is employed in amounts within the lower portion of the range, for example, about 1.0% to 1.5%. The determination of the specific maximum and optimum concentration of acid for any specific viscose, spinning bath and spinning speed is a matter of simple experimentation for those skilled in the art. The extruded viscose must, of course, be immersed or maintained in the spinning bath for a period sufficient to effect relatively complete coagulation of the viscose, that is, the coagulation must be sufficient so that the filaments will not adhere to each other as they are brought together and withdrawn from the bath.

In the production of filaments for such purposes as the fabrication of tire cord, the filaments are preferably stretched after removal from the initial coagulating and regenerating bath. From the initial spinning bath, the filaments may be passed through a hot aqueous bath which may consist of hot water or a dilute acid solution and may be stretched from about 70% to about 110%, preferably between 85% and 100%. Yarns for other textile purposes may be stretched as low as 20%. The precise amount of stretching will be dependent upon the desired tenacity and other properties and the specific type of product being produced. It is to be understood that the invention is not restricted to the production of filaments and yarns but it is also applicable to other shaped bodies such as sheets, films, tubes and the like. The filaments may then be passed through a final regenerating bath which may contain from about 1% to about 5% sulfuric acid and from about 1% to about 5% sodium sulfate with or without small amounts of sinc sulfate if regeneration has not previously been completed.

The treatment following the final regenerating bath, or the stretching operation where regeneration has been completed, may consist of a washing step, a desulfurizing step, the application of a finishing or plasticizing material and drying before or after collecting, or may include other desired and conventional steps such as bleaching and the like. The treatment after regeneration will be dictated by the specific type of shaped body and the proposed use thereof.

Regenerated cellulose filaments prepared from viscose containing the small amounts of the alkali-soluble polyoxyalkylene glycol ethers of the primary alcohols and spun in the spinning baths of limiting acid content

have a smooth or non-crenulated surface and consist substantially entirely of skin. Because of the uniformity of structure throughout the filament, the swelling and staining characteristics are uniform throughout the cross-section of the filament. Filaments produced pursuant to this invention and consisting entirely of skin have a high toughness and a greater flexing life than filaments as produced according to prior methods which may be attributed by the uniformity in skin structure through the filament. Although the twisting of conventional filaments, as in the production of tire cord, results in an appreciable loss of tensile strength, there is appreciably less loss in tensile strength in the production of twisted cords from the filaments consisting entirely of skin. Filaments prepared from viscose containing the polyoxyalkylene glycol ethers of the primary alcohols have a high tensile strength as compared to normal regenerated cellulose filaments, have superior abrasion and fatigue resistance characteristics and have a high flex-life. Such filaments are highly satisfactory for the production of cords for the reinforcement of rubber products such as pneumatic tire casings, but the filaments are not restricted to such uses and may be used for other textile applications.

The invention may be illustrated by reference to the preparation of regenerated cellulose filaments from a viscose containing about 7% cellulose, about 6% caustic soda, and having a total carbon disulfide content of about 41% based on the weight of the cellulose. The viscose solutions were prepared by xanthating alkali cellulose by the introduction of 36% carbon disulfide, based on the weight of the cellulose and churning for about 2½ hours. The cellulose xanthate was then dissolved in caustic soda solution. An additional 5% carbon disulfide was then added to the mixer and the mass mixed for about one hour. The polyoxyethylene glycol-aliphatic alcohol ether was added to the caustic soda solution and mixed for about ½ hour. The viscose was then allowed to ripen for about 30 hours at 18° C.

Example 1

Approximately 2% (based on the weight of the cellulose) of a polyoxyethylene glycol ether of technical grade, stearyl alcohol having about 100 ethylene oxide units per mole of the alcohol was added to and incorporated in the viscose as described above. The viscose employed in the spinning of filaments had a salt test of 9.4. The viscose was extruded through a spinneret at a rate of about 22 meters per minute to form a 1650 denier, 720 filament yarn for the production of a tire cord. The coagulating and regenerating bath was maintained at a temperature of about 60° C. and contained 7% sulfuric acid, 8% zinc sulfate and 17% sodium sulfate. The yarn was passed over a godet from which it was conducted to thread-advancing reels where it was stretched about 100%, washed free of acid and salts, dried and collected on cones.

The individual filaments have a smooth, non-crenulated exterior surface and consist entirely of skin, no core being detectable at high magnification (e.g. 1500×). The filaments of a control yarn spun with the same viscose but without the addition of the polyoxyethylene glycol-aliphatic alcohol ether and spun under the same conditions exhibit a very irregular and serrated surface and are composed of about 70% skin and the balance core with a sharp line of demarkation between the skin and core.

Example 2

Example 1 was repeated by spinning a viscose solution as described under the same conditions except that the filaments were stretched approximately 85% while passing between the thread advancing reels.

The individual filaments were readily distinguishable from control filaments prepared from viscose containing no modifier in that they have a smooth, non-crenulated surface and consist entirely of skin. Control filaments have a very irregular and serrated surface and consist of about 70% skin and the balance core with a sharp line of demarkation between the skin and core. The tenacity and elongation of the filaments of this example are slightly lower than that of the filaments of Example 1.

Example 3

To a viscose solution as described above, there was added 3% (based on the weight of the cellulose) of a polyoxyethylene glycol ether of decanol having about 30 ethylene oxide units per molecule. The viscose had a salt test of 8.5 and was spun into a 200 denier, 120 filament yarn by extrusion into a bath containing 7.5% sulfuric acid, 8% zinc sulfate and 19% sodium sulfate. The bath was maintained at a temperature of 60° C. The extrusion rate was about 22 meters per minute. The water bath was maintained at a temperature of 95° C. and the filaments were stretched 82% while passing through the hot water. The yarn was collected in a spinning box, washed free of acids and salts and dried.

The individual filaments had a smooth, non-crenulated surface and consist entirely of skin while control filaments have a very irregular and serrated surface and consist of 70% skin and the balance core with a sharp line of demarkation between the skin and the core.

One of the properties of viscose rayon which has limited its uses is its relatively high cross-sectional swelling when wet with water, this swelling amounting to from about 65% to about 80% for rayon produced by conventional methods. Rayon filaments produced in accordance with the method of this invention have an appreciably lower cross-sectional swelling characteristic, the swelling amounting to from about 45% to about 60%.

If desired, small amounts of the polyoxyalkylene glycol-aliphatic alcohol ether may be added to the spinning bath. Since the substances are also water-soluble, some of the modifier will be leached from the filament and will be present in the bath.

The modifier of this invention may be added to any desired viscose such as those normally used in industry, the specific viscose composition set forth above, being merely for illustrative purposes. The polyoxyethylene glycol-aliphatic alcohol ether may be added at any desired stage in the production of the viscose and may be present in the cellulosic raw material provided that the amount present will produce a viscose having the proper proportion of the ether at the time of spinning.

The term skin is employed to designate that portion of regenerated cellulose filaments which is permanently stained or dyed by the following procedure: A microtome section of one or more of the filaments mounted in a wax block is taken and mounted on a slide with Meyer's albumin fixative. After dewaxing in xylene, the section is placed in successive baths of 60% and 30% alcohol for a few moments each, and it is then stained in 2% aqueous solution of Victoria Blue BS conc. (General Dyestuffs Corp.) for 1 to 2 hours. At this point, the entire section is blue. By rinsing the section first in distilled water and then in one or more baths composed of 10% water and 90% dioxane for a period varying from 5 to 30 minutes depending on the particular filament, the dye is entirely removed from the core, leaving it restricted to the skin areas.

This application is a division of my copending application Serial No. 466,671, filed November 3, 1954, and now abandoned.

While preferred embodiments of the invention have been disclosed, the description is intended to be illustrative and it is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined by the appended claims.

I claim:

1. A viscose spinning solution containing from about 1% to about 6%, based on the weight of the cellulose in the viscose, of a substance selected from the group consisting of alkali-soluble polyoxyethylene glycol mono-ethers of higher primary aliphatic alcohols, mixtures thereof, alkali-soluble polyoxypropylene glycol mono-ethers of higher primary aliphatic alcohols and mixtures thereof, the mono-ether containing from about 20 to about 200 alkylene oxide units per molecule of alcohol, the alcohols containing from 8 to 24 carbon atoms.

2. A viscose spinning solution containing from about 2% to about 5%, based on the weight of the cellulose in the viscose, of a substance selected from the group consisting of alkali-soluble polyoxyethylene glycol mono-ethers of higher primary fatty alcohols, the mono-ether containing from about 30 to about 150 ethylene oxide units per molecule of alcohol, the alcohols containing from 8 to 24 carbon atoms.

3. A viscose spinning solution containing from about 2% to about 5%, based on the weight of the cellulose in the viscose of a polyoxyethylene glycol mono-ether of technical stearyl alcohol, the ether containing from about 30 to about 150 ethylene oxide units per molecule of alcohol.

4. A viscose spinning solution containing from about 2% to about 5%, based on the weight of the cellulose in the viscose, of a polyoxyethylene glycol mono-ether of decanol, the ether containing from about 30 to about 150 ethylene oxide units per molecule.

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