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PRODUCING ALL SKIN VISCOSE RAYON

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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 treated 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.

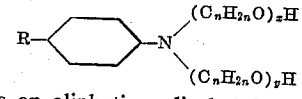
In the production of shaped bodies such as filaments, the viscose solution is extruded through a spinneret into a coagulating and regenerating bath consisting of an aqueous acid solution containing zinc sulfate and/or other salts. The filament may subsequently be passed through a hot aqueous bath where 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 the event 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 conventional 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 amounts of zinc salts or certain other salts of polyvalent metals 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 subjected to fibrillation and is relatively stiff.

It has now been discovered that the presence of small amounts of alkali-soluble alkylene oxide adducts of p-aliphatic anilines, based on the weight of the cellulose in the viscose, in a viscose which has a relatively high salt test, 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 composition of the

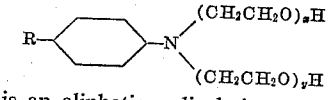
spinning bath is maintained within certain composition limits which will be defined hereinafter. The most readily distinguishable characteristics as compared to conventional filaments are that the filaments consists entirely of skin and have smooth, non-crenulated surfaces.

Various alkylene oxides such as ethylene oxide and propylene oxide may be condensed with the p-aliphatic anilines to form the polyoxyalkylene compounds contemplated in this invention. The adducts or compounds correspond to the formula



wherein R is an aliphatic radical defined hereinafter, n is 2 or 3 and x plus y is from about 6 to about 75 or more. It is obvious, however, that for all practical purposes, considering cost, ease of preparation, commercial availability and solubility in water, and alkaline solutions such as a 6% caustic solution, the ethylene oxide adducts are preferred. Accordingly, the invention will be illustrated by reference to the ethylene oxide adducts.

The structural formula for the ethylene oxide adducts is as follows:



wherein R is an aliphatic radical, i. e., a straight chain saturated or unsaturated aliphatic radical having from 6 to 24, preferbly 8 to 18 carbon atoms. R may be derived by the reduction of fatty acids found in naturally occurring fats and oils such as sperm oil, cottonseed oil, coconut oil, corn oil, soya bean, oil, palm oils, peanut oil and the like, in which case there would be present a mixture of p-aliphatic anilines wherein the aliphatic radicals correspond to the fatty acids of the fat or oil. x plus y in the above formula is from about 6 to about 75 or more. It is preferred that x plus y, i. e., the number of units of ethylene oxide units per molecule of adduct be from about 10 to 30 so that the adduct is economical to produce and readily soluble in alkaline solutions. The adducts must have a minimum alkali-solubility (the solubility being increased as more ethylene oxide is condensed with the amine) which is sufficient to dissolve the required amount of adduct in viscose. It is probable but not necessary that x equals y when the aniline compound is condensed with ethylene oxide to produce the adduct.

The term "adduct" is used herein to simplify the disclosure and description and designates a N-substituted p-aliphatic aniline formed by the reaction between an alkylene oxide and the p-aliphatic aniline wherein the alkylene oxide or the polyoxyalkylene chain replaces the hydrogen atoms attached to the nitrogen atom. These adducts may be termed N-di(omega-hydroxy polyoxyalkyl), p-aliphatic anilines wherein the aliphatic radical is a hydrocarbon chain having 6 to 24 carbon atoms and containing from about 6 to about 75 alkylene oxide units per molecule of the p-aliphatic aniline. It is not necessary to employ individual specific compounds of the type described and the reaction products which may consist of a mixture of specific compounds, the average alkylene oxide content per molecule of the p-aliphatic aniline being within the stated range, are satisfactory.

The amount of the adduct which is incorporated in the viscose must be at least about 0.2% by weight of the cellulose and may vary up to about 4%, preferably, the amount varies from about 0.5% to 2.5%. 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 adduct may be added at any desired stage in the production of the viscose, preferably being added after the cellulose xanthate has been dissolved in the caustic solution.

The composition of the viscose prior to the incorporation of the adduct is, in general, conventional in the art. 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 of this invention, i. e., a viscose containing a small amount of the alkylene oxide adduct, has a salt test above about 6 and preferably above 8 at the time of spinning or extrusion. The term "salt test" as used herein has reference to the conventional sodium chloride salt test.

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. When the modified viscose described above is extruded into the limited spinning baths defined below, yarns of improved properties such as high tenacity, high abrasion resistance, high fatigue resistance and consisting of filaments composed entirely of skin are produced.

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 containing the adducts lies between about 5% and about 8%. The acid concentration may be increased as the amount of additive or 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 modifier is increased beyond about 4% 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% carbon disulfide and 1%, based on the weight of the cellulose, of an ethylene oxide adduct of p-dodecyl aniline having about 15 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 7.5%, 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. It has been determined that the maximum permissible percentage of acid in the bath is approximately 1.30 times the percentage of caustic in the viscose and is preferably maintained between about 1.15 and 1.25 times the caustic content. 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.

The presence of the ethylene oxide adducts of the p-aliphatic aniline in the viscose retards the coagulation and, therefore, the amount of the adduct 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 adduct is employed in amounts within the lower portion of the range, for example, about 0.5%. 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 zinc sulfate if regeneration has not previously been completed.

The treatment following the final regeneration 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 adducts described herein and spun in the spinning baths of limited 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 adducts 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 is illustrated in the examples below 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 ethylene oxide adducts were added to the caustic soda solution and mixed for about one-half hour.

The percentages in the following examples are by weight including the adduct percentages which are based on the cellulose in the viscose.

Example 1

Approximately 1% of the ethylene oxide adduct of p-dodecyl aniline, containing about 20 ethylene oxide units per molecule was added to and incorporated in the viscose as described above. The viscose employed in the spinning of filaments had a salt test of 10.6. The viscose was extruded through a spinneret into a bath to form a 208 denier, 120 filament yarn at a rate of about 22 meters per minute. The coagulating and regenerating bath was maintained at a temperature of about 58° C. and contained 7.5% sulfuric acid, 8.1% zinc sulfate and 21% sodium sulfate. The yarn was passed over a godet from which it was conducted through a hot water bath maintained at about 95° C. During the travel through the hot water bath, the yarn was stretched approximately 82%. The yarn was then collected in a spinning box, washed free of acid and salts and dried.

The individual filaments formed from viscose containing the adduct had a smooth, non-crenulated exterior surface and consisted entirely of skin, no core being detectable at high magnification (e. g. 1500 ×). The yarn had a dry tensile strength of 3.4 gms. per denier and a wet tensile strength of 2.6 gms. per denier. The elongation at breaking was 22% dry and 27% wet.

Example 2

0.5% of the ethylene oxide adduct of p-dodecyl aniline, having about 15 units of ethylene oxide per molecule was added to and incorporated in the viscose as described above. The viscose had a salt test of 9.6 and was spun into a 208 denier, 120 filament yarn by extrusion into a bath containing 7.3% sulfuric acid, 7.7% zinc sulfate and 20% sodium sulfate. The bath was maintained at a temperature of 62° C. The extrusion rate was about 22 meters per minute. The yarn was stretched about 82%, washed free of acid and salts by treatment with water at about 95° C. and dried.

The individual filaments were smooth, non-crenulated and consisted entirely of skin. The yarn had a dry tensile strength of 3.0 gms. per denier and a wet tensile strength of 2.0 gms. per denier. The elongation at breaking was 24% dry and 31% wet.

In each of the above examples, control yarns were spun from viscose containing no additives but into the same controlled baths. The individual filaments of the control yarns had very irregular and serrated surfaces and consisted of from about 50 to 90% skin and from about 10 to 50% core with a sharp line of demarkation between skin and 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 adducts 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.

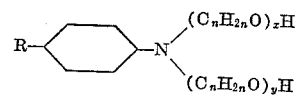
The modifier of this invention may be added to any desired viscose such as those normally used in industry, the specific viscose composition set forth above, being merely for illustrative purposes. The adducts may be added at any desired stage in the production of the viscose and may be present in the 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.

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. In a method of producing shaped bodies of regenerated cellulose consisting substantially entirely of skin by extruding viscose into a coagulating and regenerating bath, the improvement which comprises modifying the viscose by incorporating therein from 0.2% to 4%, based on the weight of cellulose in the viscose, of a water-soluble substance selected from the compounds corresponding to the formula



and mixtures of such compounds, wherein R is an aliphatic radical having from 6 to 24 carbon atoms, *n*

is at least 2 but not more than 3, x and y are whole numbers and their sum is from 6 to about 75, and extruding said modified viscose into a bath containing from about 10% to about 25% sodium sulfate, from about 3% to about 15% zinc sulfate and sulfuric acid, the percentage sulfuric acid content of the bath exceeding the slubbing point but not exceeding about 1.3 times the percentage of caustic soda in the viscose so as to produce shaped bodies consisting substantially entirely of skin, said modified viscose having a sodium chloride salt test of greater than 6 at the time of extrusion.

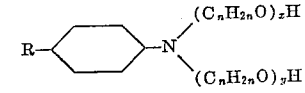
2. The steps in the method as defined in claim 1 wherein the compounds correspond to the formula as set forth in claim 1 when n is 2.

3. The steps in the method as defined in claim 1 wherein the compounds correspond to the formula as set forth in claim 1 when R is an aliphatic radical having from 8 to 18 carbon atoms, n is 2 and the sum of x and y is from 10 to 30.

4. The steps in the method as defined in claim 1 wherein the compounds correspond to the formula as set forth in claim 1 when R is the dodecyl radical, n is 2 and the sum of x and y is from 10 to 30.

5. In a method of producing filaments of regenerated cellulose consisting substantially entirely of skin by extruding viscose into a coagulating and regenerating bath, the improvement which comprises modifying the viscose by incorporating therein from 0.5% to 2.5%, based

on the weight of cellulose in the viscose, of a water-soluble substance selected from the compounds corresponding to the formula



and mixtures of such compounds, wherein R is an aliphatic radical having from 6 to 24 carbon atoms, n is at least 2 but not more than 3, x and y are whole numbers and their sum is from 6 to about 75, and extruding said modified viscose into a spinning bath containing from about 16% to 20% sodium sulfate, from about 4% to 9% zinc sulfate and sulfuric acid, the percentage sulfuric acid content of the bath exceeding the slubbing point but not exceeding 1.25 times the percentage concentration of caustic soda in the viscose so as to produce shaped bodies consisting substantially entirely of skin, said modified viscose having a sodium chloride salt test of greater than 8 at the time of extrusion.

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