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MANUFACTURE OF ARTIFICIAL FILAMENTS

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This invention relates to improvements in the production and treatment of artificial filaments, threads, yarns, ribbons and the like containing organic derivatives of cellulose, and particularly to the production of artificial materials by wet spinning processes and to the treatment of artificial materials obtained by any dry or wet spinning process.

U. S. Patents Nos. 1,465,994 and 1,467,493 describe the use, in the production of artificial filaments and the like by wet spinning processes, of aqueous coagulating baths containing solvents or latent solvents for cellulose acetate, for example thiocyanates, zinc chloride, diacetone alcohol, acetic acid and other organic or inorganic substances. British Patent No. 340,324 describes the coagulation of solutions containing organic derivatives of cellulose by means of media containing solvents for the cellulose derivative in relatively high concentration, and also processes in which the solvent is incorporated in the spinning solution itself either wholly or in part in place of the solvent in the coagulating bath, and with the treatment of the products immediately after coagulation so as to bring them into a plastic state. British Patent No. 340,324 also describes the coagulation of solutions of organic derivatives of cellulose by means of coagulating baths containing aliphatic esters or partial ethers of polyhydric alcohols, while British Patent No. 380,819 carries out the coagulation of such solutions by means of coagulating media of high solvent power containing lower aliphatic acids and high boiling solvents.

Again, in U. S. Patent No. 1,709,470 there is described the stretching of cellulose acetate silk filaments beyond their elastic limit at any stage of their manufacture after the silk is in the fully set and finished condition in order to improve their resistance to delustring by hot aqueous liquors, and it is mentioned that "assisting agents", for example, acetone, ethyl alcohol, formaldehyde and glycerine, may be employed to assist the stretching operation. Further, in British Patent No. 323,790 the stretching of artificial filaments and the like containing organic derivatives of cellulose during their travel from one point to another in order to increase their tensile strength is described, and in this case also, suitable assisting agents may be used to facilitate the stretching. French Patent No. 663,743 describes processes for improving the tensile strength of materials containing organic derivatives of cellulose in which they are treated with relatively high concentrations of organic solvents, such treatment being, if desired, carried out in conjunction with a stretching operation. The stretching of artificial filaments and the like in stages is described in British Patent No. 370,430, while British Patent No. 371,461 describes stretching processes applied to artificial filaments, threads, yarns and the like in warp form. In these cases also the stretching operation may be assisted by means of solvents for the organic derivative of cellulose.

I have now discovered that the coagulation of solutions of organic derivatives of cellulose and the stretching of artificial materials containing such derivatives, for example by any of the processes described in the above specifications, may be assisted by the use of liquid organic solvents for the cellulose derivative, preferably used in solutions of relatively high concentration, in conjunction with solid substances, which may be organic or inorganic and which have at least a slight solvent or swelling action on the cellulose derivative.

The organic solvents and solid substances are preferably employed in solution in non-solvent diluents but they may be applied in any other suitable manner. Thus, the solvent and solid substance may be applied together dissolved in a non-solvent for the cellulose derivative, which non-solvent will act as a diluent, or, where the solid substance is soluble in the organic solvent, a solution of the solid substance in the organic solvent alone may be directly employed if applied under such conditions that too strong a solvent action on the cellulose derivative does not result.

As stated above, the solid substances employed may be either organic or inorganic in nature and among suitable compounds may be mentioned urea and substitution derivatives thereof, for example s-diethyl urea, as-diethyl diphenyl urea, s-diethyl diphenyl urea, tetraphenyl urea, thiourea, s-dimethyl thiourea, guanidine and monomethyl guanidine. In addition thiocyanates, e. g. sodium and potassium thiocyanates, and zinc chloride may be employed.

The organic solvents employed may be any of those mentioned in the above specifications and may be of low, medium or high boiling point. Suitable solvents are acetone, methylene ethylene oxide, ethyl lactate, diethyl tartrate, dioxane, diacetone alcohol, 1.4-oxanone and the ethers, esters and ether-esters of polyhydroxy alcohols, e. g. mono-, di- and tri-acetins, glycol mono acetate and methyl glycol mono acetate. Such solvents may also be employed in preparing spinning solutions from which the materials are prepared. The solvents and solid substances are preferably applied in solution in diluents having themselves no solvent or swelling action on the organic derivatives of cellulose. Such diluents may be water or other hydroxy bodies, for example ethyl and other mono- or poly-hydroxy alcohols or hydrocarbons, for example benzene, toluene or other coal tar hydrocarbons, gasoline, kerosene or other petroleum hydrocarbons and

chlorinated compounds, for example carbon tetrachloride.

When the process of the present invention is applied in the coagulation of solutions of organic derivatives of cellulose such solutions may be extruded into a bath containing a solution of the solvent for the cellulose derivative and the solid substance, or one or both of the compounds, or a portion thereof, may be contained in the spinning solution or in a subsequent treatment bath. Preferably the materials are stretched continuously with their production by such wet spinning methods and in this case means may be adopted to restrict the tension applied to the materials, for example to prevent the stretching tension running back as far as the spinning jets as described in U. S. Patent No. 2,025,730. Furthermore, if desired, the stretching of the materials may be effected or assisted by means of a moving body of coagulating liquid as described in British Patent No. 375,424. Where the present invention is applied to the production of films, foils, sheets and the like the materials may be subjected to a longitudinal and/or transverse stretch as described in British Patent No. 400,597. Again, in the production of the materials whether in the form of filaments, yarns and the like or of films, foils and the like the coagulating bath may contain an organic solvent which is the same as that employed in the spinning solution from which the materials are produced. Such processes are described, for example, in British Patents Nos. 405,676, and 405,619.

In the case of stretching artificial materials the solvents and solid substances used according to the present invention are preferably applied by passing the artificial materials through a bath containing the same, though, if desired, they may be applied by other methods, for example by spraying, or by passing the materials over wicks, rollers or the like impregnated with solutions containing the media. The application of the softening agents may take place prior to or during each stage of the stretching and, if desired, the materials may be subjected to a plurality of softening treatments of different strengths as described in French Patent No. 740,775. As stated above stretching may, if desired, be carried out in a number of stages and preferably during such multi-stage stretching the softening agents are not removed between the stages of stretching. Such processes are described, for example, in British Patent No. 370,430.

The stretching operation may be carried out upon the materials in any convenient form. Thus, for example, hanks may be soaked in a solution containing the liquid organic solvent and the solid substance and then stretched. Again, the process may be carried out on the filaments or yarns during their travel from one point to another, for example continuously with their production by dry or wet spinning processes, or during a bobbin to bobbin rewinding operation as described in British Patent No. 323,790. It may very advantageously be applied to the stretching of a number of threads or yarns arranged as a warp as described in British Patent No. 371,461. Thus, for example, threads taken from a creel of bobbins may be arranged in warp formation and led through a bath containing the organic solvent and the solid substance, or the threads on bobbins may be partially softened by pre-soaking the bobbins in a bath comprising the organic solvent and the solid substance and the threads from such bobbins arranged in warp formation and led through a further bath containing the organic solvent and the solid substance. After the materials have been softened by either of the above described methods the stretch may be applied to the warp as a whole. Where the stretching operation is carried out upon films, foils, sheets and the like, the materials may be subjected to a longitudinal and transverse stretch simultaneously as described in British Patent No. 400,589.

Where the application of the softening agent and the stretching is carried out as a continuous process the stretching force may be applied directly to the softened part of the materials or it may be applied thereto after the softening agent has been removed and even after drying, since the tension may be allowed to run back to the softened portion of the materials. Advantageously means may be adopted to prevent the whole or part of the stretching tension acting upon the unsoftened or incompletely softened portion of the filaments. Such processes are described, for example, in French Patent No. 755,621.

As stated above, the solvents employed according to the present invention are preferably applied in relatively high concentration, for example concentrations of from 25 to 65%, while the concentration of the solid substance will in general be lower, for example from 2 to 5 or 10% or more. Since the solid substances employed according to the present invention have themselves some solvent or swelling action upon the organic derivative of cellulose, the proportion of liquid organic solvent employed will in general vary inversely as the proportion of solid substance.

The treatment of the materials with the organic solvent in conjunction with the solid substance may be carried out at any suitable temperatures, but preferably is effected at atmospheric temperature. The concentration necessary to effect a high degree of softening of the materials which is valuable in obtaining high degrees of stretching, will in general vary with the temperature, lower concentrations being employed with higher temperatures.

If desired, filaments, threads, yarns and the like of cellulose esters may be treated continuously with their stretching by the process of the present invention with saponifying agents so as to obtain either a product which consists partly of cellulose ester and partly of regenerated cellulose, for example a superficially saponified product, or which consists of a cellulose ester of a lower ester content, or which is substantially regenerated cellulose. By this means products may be produced having an affinity for cotton dyestuffs and a very high tensile strength. The saponification may be carried out with any suitable saponifying agent, for example aqueous caustic soda, caustic potash, trisodium phosphate and the like to which it is preferable to add sodium acetate or soaps or like buffer substances. Alcoholic solutions may be employed, for example ethyl alcohol solutions of caustic soda or caustic potash or solutions of those substances in methyl alcohol or an alcohol higher than ethyl alcohol or a glycol, glycerine or other polyhydric alcohol. Such processes are described, for example, in British Patent No. 402,104. Aqueous saponifying treatments may be carried out in the presence of lime or similar agents as described in British Patent No. 402,105. It is advantageous to carry out such saponifying treatments upon the materials whilst they are in warp formation.

The organic solvents and solid substances with which the materials are treated according to the present invention may be allowed to remain in the materials while they are subjected to the saponifying treatment, or may be removed therefrom before such treatment. The organic solvents and solid substances used, however, may assist in the saponifying treatment.

The materials may be subjected to any other further treatment in order to modify their properties, for example to alter their lustre and they may carry with them the solvents or solid substances employed according to the present invention, which may assist in such after-treatment processes. Again, effects may be produced by the local application of the solvents and/or solid substances of the present invention followed by or simultaneously with a stretching process. Thus, the solvent and/or solid substance may be locally applied to the materials and the materials then subjected to a stretching treatment. It is then found that the stretching is substantially confined to the softened parts of the filaments or other products. Again, the materials may be treated with the softening agents and subjected to a process of stretching in which the tension is applied intermittently. Means whereby differentially strained yarns may be produced are described in U. S. Patent No. 2,004,139. Furthermore, materials which have thus been differentially stretched along their length may be treated with saponifying agents to obtain differential saponifying effects along their length as described in British Patent No. 400,938, and may, moreover, be subjected to suitable delustring treatments which will produce differential delustred effects along their length as described in British Patent No. 400,946.

After a stretching operation the materials may be subjected to a shrinking operation to improve their extension. Such shrinking may be effected in the presence of the organic solvent and the solid substance employed in the stretching operation or may be effected with the aid of other solvents or strong swelling agents, for example acetic acid, formic acid, lactic acid, diacetone alcohol, acetone, dioxane, methylene ethylene oxide, 1-4-oxanone and the monoesters, di-esters or ether esters of polyolefine glycols, e. g. glycol mono acetate and ethyl glycol mono acetate, methylene chloride, dichlorethylene, ethyl lactate, and diethyl tartrate. Suitable shrinking processes are described, for example in British Patent No. 389,823. Again, the materials may be subjected to a shrinking operation prior to stretching as described in British Patent No. 403,106.

After the process of the present invention the organic solvent and the solid substance employed may be removed by any suitable means. In order to preserve the lustre of the materials it is desirable, especially if the agents have been applied in high concentrations, to remove the agents by washing with water, or other liquid, containing either the same agent or another solvent or softening agent in lower concentration than that employed in the softening treatment, or to wash with liquids containing salts or other agents adapted to prevent or diminish loss of lustre. It is particularly useful to wash the materials with media comprising solvents for the materials which are less volatile than the solvents which are to be removed. Again, the softening liquid or a portion thereof may itself be employed for washing the materials, for example as described in British Patent No. 401,679. Advantageously the materials are subjected to two or more washings with such solutions of successively decreasing concentrations. The materials may be dried whilst they are under tension or in the absence of tension and the drying operation may be carried out when all the softening agent has been removed from the materials or when the materials still contain a portion of the softening agent. Thus, drying may be effected under such conditions that shrinkage is prevented, or under such conditions that a desired amount of shrinkage is allowed to take place. Where the solid substance is not deleterious to the materials, and where it is of advantage to leave it in or upon the materials, the organic solvent may simply be evaporated from the materials, leaving the solid substance in situ.

The following examples serve to illustrate the invention, but they do not, of course, limit it in any way:—

Example 1

A 25% solution of cellulose acetate is spun through orifices .08 mm. diameter into a bath containing 5% by weight of potassium thiocyanate, 45% by weight of diacetone alcohol and 50% by weight of water. After a travel through this bath of a distance of 8–10 inches the filaments are withdrawn by means of a draw roller at a speed of 50 metres per minute. After removal of the solvent and the solid substance by a suitable washing operation, the materials are dried and wound or twisted and wound.

Example 2

The process described in Example 1 is carried out except that the solution of cellulose acetate is extruded into an aqueous bath containing 2.5% by weight of urea and 47.5% by weight of ethyl lactate. In this process the urea not only assists in the coagulation of the filaments, but also assists in preventing the coagulating bath from becoming acid.

In each of the above examples the ratio of the peripheral speed of the draw roller to the rate of extrusion may be such that the filaments are stretched, e. g. by 200%–300% or more.

Example 3

A number of cellulose acetate threads are led from a creel of bobbins through a reed or other spacing device and in the form of a warp are led under a feed roller and immersed into an aqueous bath containing 2.5–3.5% by weight of urea and 46.5–47.5% by weight of dioxane. After a travel of between 80 and 100 feet the threads are withdrawn from the bath through another reed by means of a stretching roller which rotates at such a speed as to effect a stretch of about 400 to 500% on the original length of the threads. The warp of threads issuing from the bath is led through suitable washing baths and the threads are then dried and wound in any suitable manner.

The process of the present invention is of particular value in connection with artificial filaments, threads, ribbons and the like containing cellulose acetate, but it may also be applied to other organic esters or mixed esters of cellulose, for example cellulose formate, propionate, butyrate and nitroacetate, methyl, butyl, benzyl and other cellulose ethers or mixed ethers and cellulose ether-esters, for example oxyethyl cellulose acetate and ethyl cellulose acetate.

What I claim and desire to secure by Letters Patent is:—

1. In the manufacture of artificial filaments, yarns, threads, ribbons, foils, films and the like from solutions of organic derivatives of cellulose, the steps of extruding a solution of an organic derivative of cellulose through a suitable shaping device into a coagulating medium containing in a non-solvent diluent a concentration of 25 to 65% of a liquid organic solvent for the cellulose derivative and a proportion of 2 to 10% of the medium of an organic substance which is normally solid and has at least a slight swelling action on the cellulose derivative, and subjecting the materials to a stretching operation.

2. In the manufacture of artificial filaments, yarns, threads, ribbons, foils, films and the like from solutions of cellulose acetate, the steps of extruding a solution of cellulose acetate through a suitable shaping device into an aqueous coagulating medium containing a concentration of 25 to 65% of a liquid organic solvent for the cellulose acetate and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives, which has at least a slight swelling action on the cellulose acetate, and subjecting the materials to a stretching operation.

3. In the manufacture of artificial filaments, yarns, threads, ribbons, foils, films and the like from solutions of organic derivatives of cellulose, the steps of extruding a solution of an organic derivative of cellulose into an aqueous coagulating medium containing a concentration of 25 to 65% of a liquid organic solvent for the cellulose derivative and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives which has at least a slight swelling action on the cellulose derivative, and subjecting the materials to a stretching operation.

4. In the manufacture of artificial filaments, yarns, threads, ribbons, foils, films and the like from solutions of cellulose acetate, the steps of extruding a solution of cellulose acetate through a suitable shaping device into an aqueous coagulating medium containing from 25–65% of a liquid organic solvent for the cellulose acetate and from 2–10% of urea, and subjecting the materials to a stretching operation.

5. In the treatment of artificial filaments, yarns, threads, ribbons, foils, films and like products containing organic derivatives of cellulose, the steps of softening the products by the action of a liquid medium containing in a non-solvent diluent a concentration of 25 to 65% of a liquid organic solvent for the cellulose derivative and a proportion of 2 to 10% of the medium of an organic substance which is normally solid and has at least a slight swelling action on the cellulose derivative, and subjecting the products to a stretching operation.

6. In the treatment of artificial filaments, threads, yarns, ribbons, foils, films and like products containing cellulose acetate, the steps of softening the products by the action of an aqueous medium containing a concentration of 25 to 65% of a liquid organic solvent for the cellulose acetate and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives, which has at least a slight swelling action on the cellulose acetate, and subjecting the products to a stretching operation.

7. In the treatment of artificial filaments, yarns, threads and like products containing cellulose acetate, the steps of softening a number of the products arranged in warp formation by the action of a liquid medium containing in a non-solvent diluent a concentration of 25 to 65% of a liquid organic solvent for the cellulose acetate and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives, which has at least a slight swelling action on the cellulose acetate, and subjecting the products to a stretching operation.

8. In the treatment of artificial filaments, threads, yarns, ribbons, foils, films and like products containing organic derivatives of cellulose, the steps of softening the products by the action of an aqueous coagulating medium containing from 25–65% of a liquid organic solvent for the cellulose derivative and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives which has at least a slight swelling action on the cellulose derivative, and subjecting the products to a stretching operation.

9. In the treatment of artificial filaments, threads, yarns, ribbons, foils, films and like products containing cellulose acetate, the steps of softening the products by the action of an aqueous medium containing from 25–65% of a liquid organic solvent for the cellulose acetate and from 2–10% of urea, and subjecting the products to a stretching operation.

10. In the manufacture of artificial filaments, yarns, threads, ribbons, foils, films and the like from solutions of organic derivatives of cellulose, the steps of subjecting the shaped materials to the action of a liquid medium containing in a non-solvent diluent a concentration of 25 to 65% of a liquid organic solvent for the cellulose derivative and a proportion not more than of the order of 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives which has at least a slight swelling action on the cellulose derivative, and subjecting the materials to a stretching operation.

11. In the manufacture of artificial filaments, yarns, threads, ribbons, foils, films and the like from solutions of organic derivatives of cellulose, the steps of extruding a solution of an organic derivative of cellulose through a suitable shaping device into a coagulating medium containing in a non-solvent diluent a concentration of 25 to 65% of a liquid organic solvent for the cellulose derivative and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives which has at least a slight swelling action on the cellulose derivative, and subjecting the materials to a stretching operation.

12. In the treatment of artificial filaments, yarns, threads, ribbons, foils, films and like products containing organic derivatives of cellulose, the steps of softening the products by the action of a liquid medium containing in a non-solvent diluent a concentration of 25 to 65% of a liquid organic solvent for the cellulose derivative and a proportion of 2 to 10% of the medium of a substance selected from the group consisting of urea and its solid substitution derivatives which has at least a slight swelling action on the cellulose derivative, and subjecting the products to a stretching operation.

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