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## MANUFACTURE AND TREATMENT OF FILAMENTS AND THE LIKE

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This invention relates to the manufacture and treatment of artificial filaments, yarns, ribbons, and the like, and more particularly to such materials made of or containing cellulose acetate or other organic derivatives of cellulose.

In U. S. Patent No. 1,709,470 and in British Patent No. 323,790, processes are described for stretching formed filaments or other products either continuously with their production or subsequent thereto, the stretching being facilitated by previous or simultaneous treatment with solvents or swelling agents for the cellulose acetate or other cellulose derivatives. In British Patent No. 370,430, it is shown that the time factor in the treatment of the filaments or other products with the solvent or swelling agent is of considerable importance in promoting the stretching and that there is an optimum time for each cellulose derivative considered in relation to any particular solvent or swelling agent.

I have now found that filaments, yarns, threads and the like which are much more amenable to such stretching treatments, particularly when solvents or swelling agents are used to facilitate the stretching, may be obtained from spinning solutions containing a substance or substances not removed therefrom during the spinning operation, so that the said substance may be dissolved out or otherwise removed after the spinning operation is complete. In dry spinning operations, in respect of which the present invention is of greatest importance, the selected substance for addition to the spinning solution will of course be relatively non-volatile so that it remains in the filaments after spinning is finished and the filaments or other products are in condition for being wound up. In wet spinning operations, on the other hand, the substance or the coagulating bath should be so chosen that the former does not dissolve to any substantial extent in the latter.

The substance selected may be either a solvent or a non-solvent for the cellulose acetate or other basic substance comprising the filaments, yarns and the like, and may be either liquid or solid at ordinary temperatures. Substances which I have found of value in connection with cellulose acetate and similar organic derivatives of cellulose are glycerine, cyclohexanol, cyclohexanyl acetate, methyl cyclohexanol, methyl cyclohexanyl acetate, cyclohexanone, methyl cyclohexanone, cyclobutanone, acetyl acetone, the ethers, and particularly the less volatile ethers, of olefine and polyolefine glycols, for instance the monomethyl, ethyl and butyl ethers of ethylene and diethylene glycol, benzyl alcohol, benzyl acetate, ethyl oxybutyrate, diacetin, triacetin, tribenzoyl glycerine, triphenyl and tricresyl phosphates, diethyl and dibutyl phthalates, and diethyl and dibutyl tartrates, paratoluene sulphonamide and sulphoanailide, and sulphonamides and sulphonanilides in general, oils, for example hydrocarbon oils and animal or vegetable oils, and fats and waxes. Such substances may all be incorporated in solutions of cellulose acetate in acetone for spinning by dry spinning methods. Again the substances or classes of substances mentioned in British Patent No. 400,180, to which reference is made broadly, may also be employed. The substance chosen, in addition to having the properties referred to above, is preferably soluble in the spinning solution, since otherwise it is necessary to disperse it finely in order to enable it to pass the filters and spinning nozzles without unduly obstructing the same, and in order to obtain to the full the increased permeability and amenability to subsequent processing characteristic of the invention.

The substance or substances may be incorporated in the filaments or other products in any suitable proportion. Proportions of 1–5 up to 10 or 15% on the cellulose acetate or other base of the filaments produces a considerably increased permeability or amenability of the products to subsequent processing. Proportions up to 25% or more may however be used.

After the spinning operation is complete and the filaments, yarns, ribbons or the like containing the said substance have been produced, they may be subjected to any suitable operation for removing the said substance either wholly or in part. Such treatment may or may not be continuous with the spinning operation. Treatments with liquids which dissolve the said substances are in general the most convenient, and it is advisable to use a liquid which at the most has only a restricted solvent action upon the substance, such as cellulose acetate, constituting or contained in the filaments. However, the liquid chosen may, and often advantageously does, exhibit a swelling action towards the cellulose derivative or other base. In the case of cellulose acetate and similar cellulose derivatives which are soluble in acetone or in mixtures of benzene and alcohol or in ethyl acetate, hydrocarbon liquids or alcohols are very convenient for dissolving out the substance contained in the filaments. Such liquids may be mixed with solvents, for example acetone, ethyl and methyl acetate, methylene chloride or

ethylene chloride in order to promote the solvent action thereof upon the contained substance. In the case of materials produced by wet spinning processes, relatively volatile substances which are substantially insoluble in the coagulating medium may be employed, the substances being removed from the materials by the action of heat. The evaporation of the substances may be assisted by passing a current of air or inert gas over or through the materials. The filaments, yarns, ribbons and the like thus produced are novel products, and as already indicated, are particularly adapted for subsequent processing, especially stretching.

As in British Patent No. 323,790, the stretching may be facilitated by means of solvents or swelling agents, for example thiocyanates, acetone, methyl-ethel-ketone, phenols (though these are less preferable), hot alcohols, the mono- and di-ethers or esters or ether-esters of olefine and polyolefine glycols, for example mono-methyl and ethyl ethers of ethylene glycol or di-ethylene glycol, glycol mono-acetate and methyl glycol mono-acetate, dioxane and the homologues of dioxane referred to in British Patent No. 391,828, the cyclic ethers of glycerine or other polyhydric alcohols and their esters and ethers (see U. S. Patents Nos. 2,025,044 and 2,031,594, and British Patent No. 396,761, formaldehyde or other aldehydes or dichlorethylene, trichlorethylene, ethylene chloride, methylene chloride, chloroform and like chlorinated hydrocarbons, formic acid, acetic acid, lactic acid and like organic acids having a solvent action, diacetone alcohol, diethyl tartrate, ethyl lactate, or the like or mixtures of any of these or solvent mixtures. In many cases, particularly if the agent used is a true solvent or is very close to a true solvent, as for instance with methylene chloride or chloroform in treating acetone-soluble cellulose acetate, it is desirable to mix the agent with a diluent, for example benzene or other hydrocarbons, or non-solvent halogenated hydrocarbons such as carbon tetrachloride, or water, or with relatively weak swelling agents, such as alcohols. The softening treatment may be carried out with vapours of solvents or softening agents, diluted or not with air or other gases or with vapours of non-solvents.

If the liquid used to eliminate the substance contained in the filaments is itself a relatively strong swelling agent for the cellulose acetate or other base of the filaments, it may be unnecessary even in order to obtain high degrees of stretching, such as 300, 400 or 500% or more, to treat again with a swelling agent, the stretching operation being for example continuous with the removal of the substance with the aid of a liquid having swelling properties. Where such a subsequent swelling treatment is resorted to, the swelling may take place either previous to or simultaneously with the stretching operation, and by reason of the intrinsic character of the filaments produced according to the invention it is found that the softening of the filaments is very much facilitated and that the optimum time for soaking referred to above may be reduced.

The stretching may be effected where the filaments, yarns, etc. are in hank form as described in U. S. Patent No. 1,709,470, or may be conducted on the travelling filaments or yarns as described in British Patent No. 323,790. Intermittent stretching as described in British Patent No. 370,430 may be employed. In such intermittent stretching the whole of the softening required may be imparted to the filaments or other products prior to the first stage of stretching, or additional softening treatments may be applied between or during the stages of stretching.

The following examples illustrate the invention but are not to be regarded as limiting it in any way.

*Example 1*

A 22–24% solution of cellulose acetate in 95% aqueous acetone, containing 10% of triphenyl phosphate calculated on the weight of the cellulose acetate, is spun through orifices of .08 mm. diameter into an evaporative atmosphere maintained at a temperature of 75°–85° C. The filaments produced are wound or twisted and wound in any suitable manner, e. g. by means of a cap spinning apparatus. The triphenyl phosphate is then removed from the materials by passing them through a bath of benzene at a temperature of 40°–50° C., or by soaking them in package form in the bath. After removal of the triphenyl phosphate the filaments are subjected to a stretching operation, e. g. as described in U. S. Patent No. 1,709,470 and British Patents Nos. 323,790 and 370,430.

*Example 2*

A 23–25% solution of cellulose acetate in 95% aqueous acetone, containing 8–12% of diethylene glycol mono butyl ether based on the weight of the cellulose acetate, is spun through suitable orifices into an evaporative medium at a temperature of 75°–85° C. After issuing from the spinning cell the filaments are passed through a bath of 40% aqueous acetone, to remove the butyl ether and to soften them. They are then stretched, e. g. to 200–300 or 400% or more of their original length.

*Example 3*

100 parts of viscose contaning about 6–8% of cellulose and 6–8% of caustic soda and about 1% of decahydronaphthalene in a finely dispersed form are spun into a precipitating bath containing sulphuric acid and sodium sulphate. The filaments obtained are then treated with benzene at the boiling point in order to remove the decahydronaphthalene.

In addition to facilitating subsequent stretching operations, the new filaments and other products of the present invention are in general more amenable to many operations which involve treatment with liquids, for example dyeing, printing, discharging, mordanting, loading, delustering, e. g. with hot or boiling soap or other aqueous liquors, and crêping, and even many operations which do not necessarily involve liquid treatments, e. g. twisting operations, and particularly the insertion of high twist for crêpe purposes. In the insertion of twist for crêpe purposes very good results are obtained by inserting the twist in two or more stages and by applying previous to the whole twist or previously or intermittently in stage twisting water or other liquid adapted to consolidate the individual filaments of the thread. The filaments and the like of the present invention are considerably improved from this aspect. Again, filaments and the like having a more bulbous or otherwise modified cross-section may be obtained, as is described in British Patent No. 400,180.

The invention has been described above particularly in relation to cellulose acetate, but is also of especial value in the manufacture and treatment of other base materials which are relatively resistant to the penetration of aqueous or

other liquids, as for example cellulose formate, cellulose propionate, cellulose butyrate, nitro-acetate or methyl, ethyl or benzyl cellulose, and may also be applied to the manufacture and treatment of other types of artificial silk, as for instance the viscose, cuprammonium and nitrocellulose silks.

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

1. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materals, which comprises treating such materials having a base of organic derivative of cellulose and containing an additional substance which is not a solvent for the base of the materials and which is readily removable therefrom, so as to remove said substance, at least in part, and replace it by a softening liquid, and stretching the materials in the softened condition.

2. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises treating such materials having a base of cellulose acetate and containing an additional substance which is not a solvent for the base of the materials and which is readily removable therefrom, so as to remove said substance, at least in part, and replace it by a softening liquid, and stretching the materials in the softened condition.

3. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises treating such materials having a base of organic derivative of cellulose and containing an additional substance which is not a solvent for the base of the materials and which is readily removable therefrom, so as to remove said substance, at least in part, immediately thereafter softening the materials by treatment with a softening liquid, and stretching the materials in the softened condition.

4. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises treating such materials having a base of cellulose acetate and containing an additional substance which is not a solvent for the base of the materials and which is readily removable therefrom, so as to remove said substance, at least in part, immediately thereafter softening the materials by treatment with a softening liquid, and stretching the materials in the softened condition.

5. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises forming such materials from a solution having a base of organic derivative of cellulose and containing an additional substance which is not a solvent for the base of the materials and which is readily removable from the formed materials, removing at least a part of said substance from the formed materials and replacing it by a softening liquid, and stretching the materials in the softened condition.

6. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises forming such materials from a solution having a base of cellulose acetate and containing an additional substance which is not a solvent for the base of the materials and which is readily removable from the formed materials, removing at least a part of said substance from the formed materials and replacing it by a softening liquid, and stretching the materials in the softened condition.

7. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises forming such materials from such solutions, having a base of organic derivative of cellulose and containing an additional substance which is not a solvent for the base of the materials and which is readily removable from the formed materials, removing at least a part of said substance, immediately thereafter softening the materials by treatment with a softening liquid, and stretching the materials in the softened condition.

8. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises forming such materials from such solutions, having a base of cellulose acetate and containing an additional substance which is not a solvent for the base of the materials and which is readily removable from the formed materials, removing at least a part of said substance, immediately thereafter softening the materials by treatment with a softening liquid, and stretching the materials in the softened condition.

9. The process which comprises forming from a solution of cellulose acetate and triphenyl phosphate in acetone, filaments, threads, yarns, ribbons and like materials having a base of cellulose acetate and containing triphenyl phosphate, removing at least a part of the triphenyl phosphate from the formed materials by treating said materials with benzene, immediately thereafter softening the materials by treatment with a softening liquid, and stretching the materials in the softened condition.

10. The process which comprises forming from a solution of cellulose acetate and diethylene glycol mono-butyl ether in acetone, filaments, threads, yarns, ribbons and like materials having a base of cellulose acetate and containing diethylene glycol mono-butyl ether, removing at least a part of the diethylene glycol mono-butyl ether from the formed materials by treating said materials with aqueous acetone, thereby softening the materials, and stretching the materials in the softened condition.

11. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises treating such materials, having a base of organic derivative of cellulose and containing an additional substance which is not a solvent for the base of the materials and which is readily removable therefrom, with a liquid adapted to remove at least a part of said additional substance and to soften the materials, and stretching the materials in the softened condition.

12. Process for the manufacture of strong filaments, threads, yarns, ribbons and like materials, which comprises treating such materials, having a base of organic derivative of cellulose and containing an additional substance which is not a solvent for the base of the materials and which is readily removable therefrom, so as to remove said substance, at least in part, and replace it by a softening liquid, and stretching the materials in the softened condition by at least 200% of their original length.

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