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MANUFACTURE AND TREATMENT OF ARTIFICIAL SILK AND LIKE PRODUCTS

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This invention relates to the manufacture and treatment of filaments, threads, ribbons or other materials made of or containing cellulose acetate or other cellulose esters or ethers.

In the manufacture and treatment of artificial silk or other products and fabrics and other materials containing the same, it is frequently necessary to treat the products or materials with a solvent or swelling agent for the cellulose derivative. Thus, for instance, in order to decrease or obviate the tendency of woven fabrics to slip, of warp knitted fabrics to split, and of tricot or circular knitted fabrics to ladder, the fabrics may be treated with substances which are solvents or swelling agents for the cellulose derivative (compare U. S. application S. No. 152,516 filed 3rd December, 1926). Moreover solvents are employed in the relustring of materials which have been delustred, for example with hot aqueous liquids or steam (see for instance U. S. Patent No. 1,808,098). Again in the manufacture of crêpe fabrics it is often of great assistance in the production of the crêpe figure to treat the material at some stage of its manufacture, e. g. before or after twisting of the yarn, with solvents or swelling agents, (see U. S. application S. No. 501,461 filed 10th December, 1930). Furthermore, in the stretching of artificial filaments, yarns and other products the stretching is assisted very considerably by means of solvents or swelling agents, and reference is made in this connection to U. S. Patent No. 1,709,470 and U. S. application S. No. 378,684 filed 16th July, 1929. The solvent or swelling agent may, for example, be applied before or during stretching or before or during any stage of the stretching. Again, U. S. application S. No. 403,140 filed 28th October, 1929, describes processes wherein the extension of artificial filaments or other products is improved by treatment with swelling agents without stretching. Again, in U. S. application S. No. 611,240 filed 13th May, 1932 processes are described for improving the extension of high tenacity filaments, yarns or threads, for instance those obtained by wet spinning processes or those obtained by dry spinning processes with subsequent stretching, the said processes involving a treatment of the materials with solvents or swelling agents to bring about a longitudinal shrinkage. Lastly, in U. S. application S. No. 402,785 filed 26th October, 1929, processes are described in which solutions containing cellulose derivatives are coagulated in solutions containing high concentrations of solvents, and also processes in which products after leaving the coagulating medium are treated with such solutions.

The present invention relates to improvements in all such processes wherein it is required to treat the filaments, yarns, threads, ribbons, films or other products with solvents or swelling agents. I have found that in all such processes improved results may be obtained by treating the filaments, yarns or other products, carrying a mixture of a solvent or swelling agent and a non-solvent, with an agent which decreases or tends to decrease the solubility of the solvent in the non-solvent. Such agents are, for example, salts and sugars. I have found that a subsequent treatment with such agents considerably enhances the effect of the solvent or swelling agent and enables a much higher degree of softening or plasticity to be induced with the same concentration of solvent or swelling agent, or enables the solvents or swelling agents to be used in a lower concentration while producing the effect of the higher concentration.

The invention is of greatest importance when applied to the stretching of artificial silk filaments, threads, yarns and the like, and will be described with reference thereto, though it will be appreciated that a large number of other applications of the principle of the invention are possible, for instance those specified above. As solvents or swelling agents for use in the present invention the organic solvents are the most important, for example acetic acid, formic acid, lactic acid, diacetone alcohol, ethyl lactate, diethyl tartrate, acetone and the like; the mono- and di-ethers or esters and ether-esters of olefine and polyolefine glycols, for instance the mono- and di-methyl and ethyl ethers of ethylene glycol, dioxane, the mono- and di-acetyl derivatives of ethylene glycol, methyl and ethyl glycol monoacetate and the corresponding compounds of propylene glycol and of diethylene glycol; phenols, mono- and di- and tri-acetins, dichlorethylene, methylene chloride, ethylene chloride, methyl acetate, ethyl acetate, and the like. Such solvents may be employed for the purpose of the present invention in conjunction with any desired non-solvent, for example water, alcohols, for instance methyl, ethyl, iso-propyl or amyl alcohol, the glycols and glycerine, with ethers, for instance iso-propyl ether, with hydrocarbons, for instance benzene, toluene, xylene and other aromatic hydrocarbons, hexahydro-benzene, tetrahydro-naphthalene or other cycle-paraffins or hydrogenated aromatic hydrocarbons, kerosene, naphtha or other aliphatic hydrocarbons or mix-

tures thereof or chlorinated hydrocarbons, for instance carbon tetrachloride. Water and hydrophilic liquids, such as alcohols, are however the most important diluents for use in the present invention.

As the agents for reducing the solubility of the solvent or swelling agent in the non-solvent medium, salts are most important. Preferably salts are employed, whose aqueous solutions do not exert a swelling action upon the cellulose derivative and which are not seriously hydrolyzed in aqueous solution. Such salts may for example be sodium sulphate, sodium chloride, sodium acetate, sodium nitrate and sodium phosphate; ammonium sulphate, ammonium chloride, ammonium nitrate and potassium sulphate, potassium chloride, potassium nitrate, potassium acetate and potassium phosphate. The best results appear to be obtained with sodium acetate, sodium chloride, ammonium nitrate and potassium acetate, when using water as the non-solvent diluent in which the solvent or swelling agent is applied. The salts may be employed in any desired concentration, the best results being obtained with practically saturated solutions, though a good increase of the solvent power of the solvent or swelling agent employed is obtained with concentrations much lower than that corresponding to saturation point, for example concentrations of 1 to 5 or 10%. The present invention has the advantage, as compared with a process in which the salt is employed in the same bath as the solvent or swelling agent, that the salt may be employed in much higher concentration, and hence increases the effect of the solvent or swelling agent to a much greater extent.

A further class of bodies which may be used in accordance with the present invention for the purpose of improving the effect of the solvent or swelling agent in the stretching operation consists, as already indicated, of the sugars and other polyhydric alcohols, for example glucose, fructose, sucrose, xylose, mannitol, sorbitol, cellobiose, γ-cellulose or other soluble degradation or depolymerization products of cellulose.

As with the salts referred to above the sugars and other polyhydric alcohols may be used in any concentration up to saturation point, and in common with the salts, their application subsequent to the application of the solvent or swelling agent has the advantage as compared with a simultaneous application that the solvent power of the solvent or swelling agent is increased much more.

The salts, sugars and other substances adapted to decrease the solubility of the solvent in the non-solvent medium may be applied to the materials in any suitable medium. Preferably the same medium is employed as is employed to dilute the solvent, and as explained above water or a hydrophilic diluent, such as alcohol, is the most valuable.

In the application of the present invention to the stretching of artificial silk filaments, yarns, threads, ribbons and the like the solvent or swelling agent is applied to the materials first and subsequently the salt, sugar or other agent. The stretching may be effected while the material is in the form of hanks or while it is travelling from point to point, as for example from bobbin to bobbin, or from a spinning machine, e. g. a dry spinning apparatus, to a winding apparatus or while the yarns, threads and the like are in warp formation. The stretching may be effected in a number of stages, for example 2, 3, 4, 5 or more stages, the amount of stretch applied to the filaments or other products being suitably proportioned as between the stages. With a small degree of stretch at each stage, a very large number of stages may be used, and in fact the whole of the stretch may be inserted as a very gradual operation. In applying stretch in a number of stages it is also advantageous to allow a rest period between at least some of the stages, and preferably between the first and second and between the second and third stages of stretching. Reference is made in this connection to U. S. application S. No. 573,424 filed 6th November, 1931. Suitable apparatus for effecting such a stretching in stages is described in the said specification.

The solvent or swelling agent, suitably diluted with a non-solvent medium, may be applied to the materials or other products before or during the stretching or before or during any stage of the stretching, and the salt, sugar or other reagent may be applied subsequently and before or during the stretching or before or during any stage of the stretching. For instance, filaments, yarns, threads or the like may be carried through a bath containing the diluted solvent or swelling agent, round a suitable roller and stretched between this roller and a second roller rotating at a high peripheral speed. The salt, sugar or like agent may be applied to the filaments while they are on the first roller or while they are travelling between the first and second rollers.

Local stretching or differential stretching may be achieved when working according to the present invention by applying the solvents or swelling agents and/or the salts, sugars or the like substances locally to the materials, for example intermittently along the length of filaments, threads and the like. When the solvent or swelling agent is applied uniformly differential stretching may be effected by locally increasing the effect of such agent by application of salts, sugars and the like to selected places.

In its application to the wet spinning of artificial fibres according to the processes of U. S. Patents Nos. 1,465,994 and 1,467,493 and U. S. application S. No. 402,785 the materials, after leaving the coagulating bath or subsequent treatment bath, may be carried directly into a bath containing the salt, sugar or the like and a stretch or further stretch applied to the materials while they are in such bath.

After the treatments with the solvents or swelling agents, it is desirable to remove such agents from the yarn or other material, since by reason of the process of the present invention such agents are present under conditions in which they are exerting a strong solvent action upon the materials. Their removal may be effected by simple washing or by any other suitable process, but it is found that for the purpose of retaining the lustre of the goods it is desirable to wash either with a further solution of a salt or with a solution of the solvent or swelling agent in a lower concentration than that in which it is present on the materials.

The invention is of particular importance in the manufacture and treatment of filaments, yarns or other products of cellulose acetate, but it may also be applied with valuable results to the manufacture and treatment of products of other cellulose esters and mixed esters, for ex-

ample cellulose formate, cellulose propionate, cellulose butyrate and nitroacetate, of cellulose ethers and mixed ethers, for instance ethyl, butyl or benzyl cellulose, and mixed ether-esters, e. g. ethyl cellulose acetate and oxy-ethyl cellulose acetate.

The following examples are given to illustrate the invention but it is to be clearly understood that they do not limit it in any way:—

Example 1

A 25% solution of cellulose acetate in acetone is extruded through spinning nozzles having jet orifices of .08 mm. diameter into a coagulating bath containing 40 parts by weight of ethyl lactate and 60 parts by weight of water. The filaments are carried from this bath into another containing a 30% solution of sodium chloride, and then round a feed roller rotating at a peripheral speed of from 50–100 metres per minute so that a stretch is exerted. They are then washed with water or a solution of sodium chloride and collected by means of a centrifugal spinning box, a cap spinning apparatus or in any other suitable manner.

Example 2

A 26% solution of cellulose acetate in acetone is extruded through jets having orifices of about .08 mm. diameter into an evaporative atmosphere maintained at a temperature of about 70°–80° C. The filaments are carried round a feed roller into a bath containing a 45% solution of diacetone alcohol in ethyl alcohol and then into a second bath containing a 20% solution of sodium acetate in a 20:80 mixture of ethyl alcohol and water. The materials are then passed round a roller rotating at such a speed that a stretch is exerted upon them, and are finally washed and collected in any suitable manner.

Example 3

A cellulose acetate yarn in hank form is soaked for about five minutes in a 50% aqueous solution of methyl glycol monoacetate and then for from 5–10 minutes in a 70% aqueous solution of glucose. It is then submitted to a stretching operation and afterwards washed.

The following example illustrates the treatment of fabrics to improve their properties.

Example 4

A cellulose acetate knitted or woven fabric is treated for about 10 minutes in a 20% solution of acetone in water and then for a similar period in an 80% solution of ammonium nitrate. It is then removed, washed with water or a solution of ammonium nitrate, and finally dried or subjected to any other desired after-treatment process.

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

1. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, fabrics and like materials having a basis of organic derivatives of cellulose, the step of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose derivative, with a solution which contains at least 1% concentration of a salt and which decreases the solubility of said solvent in said non-solvent.

2. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, and like materials having a basis of organic derivatives of cellulose, the steps of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose derivative, with a solution which contains at least 1% concentration of a salt and which decreases the solubility of said solvent in said non-solvent, and subjecting the so-treated materials to a stretching operation.

3. In a process for the manufacture of artificial filaments, threads, yarns, ribbons and like materials having a basis of organic derivatives of cellulose, the steps of treating such materials while they are carrying a solution of a solvent in a hydrophilic non-solvent for the cellulose derivative with a solution which contains at least 5% concentration of a salt and which decreases the solubility of said solvent in said non-solvent, and subjecting the so-treated materials to a stretching operation.

4. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, fabrics and like materials having a basis of organic derivatives of cellulose, the step of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose derivative, with a substantially saturated solution of a salt which reduces the solubility of said solvent in said non-solvent.

5. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, fabrics and like materials having a basis of organic derivatives of cellulose, the steep of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose derivative, with a solution which contains, in at least 5% concentration an organic salt which is non-hydrolyzed in aqueous liquids, and which reduces the solubility of said solvent in said non-solvent.

6. In a process for the manufacture of artificial filaments, threads, yarns, ribbons and like materials having a basis of organic derivatives of cellulose, the steps of treating such materials, while they are carrying an aqueous solution of a solvent for the cellulose derivative, with a substantially saturated aqueous solution of an inorganic salt which is non-hydrolyzed in aqueous liquids and which reduces the solubility of said solvent in water, and subjecting the so-treated materials to a stretching operation.

7. In a process for the manufacture of artificial filaments, threads, yarns, ribbons and like materials having a basis of cellulose acetate, the steps of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose acetate, with a solution which contains, in at least 5% concentration, an inorganic salt which is non-hydrolyzed in aqueous liquids and which reduces the solubility of said solvent in said non-solvent, and subjecting the so-treated materials to a stretching operation.

8. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, fabrics and like materials having a basis of cellulose acetate, the step of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose acetate, with a substantially saturated solution of an alkali metal salt of acetic acid.

9. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, fabrics and like materials having a basis of cellulose acetate, the step of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose acetate, with a substantially saturated solution of sodium chloride.

10. In a process for the manufacture of artificial

filaments, threads, yarns, ribbons, fabrics and like materials having a basis of cellulose acetate, the step of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose acetate, with a substantially saturated solution of ammonium nitrate.

11. In a process for the manufacture of artificial filaments, threads, yarns, ribbons and like materials having a basis of organic derivatives of cellulose, the step of treating such materials while they are carrying a solution of a solvent in a non-solvent for the cellulose derivative, with a solution which contains, in at least 5% concentration, an inorganic salt which is non-hydrolyzed in aqueous liquids, and which reduces the solubility of said solvent in said non-solvent, subjecting the so-treated materials to a stretching operation, and thereafter washing the materials with a solution of the said inorganic salt.

12. Process for the treatment of artificial filaments, threads, yarns, ribbons and like materials having a basis of organic derivatives of cellulose, which comprises treating the said materials with a medium comprising a solution of a solvent in a non-solvent for the cellulose derivative, subjecting the materials while carrying a solution of said solvent in said non-solvent to the action of a solution which contains at least 5% concentration of a salt and which decreases the solubility of said solvent in said non-solvent, and subjecting the materials to a stretching operation.

13. Process for the manufacture of artificial filaments, threads, yarns, ribbons, and like materials, which comprises extruding a solution having a basis of an organic derivative of cellulose into a coagulating bath containing a solution of a solvent for the cellulose derivative in a non-solvent therefor, subjecting the products issuing from said bath and while they are carrying a solution of said solvent in said non-solvent to the action of a solution which contains at least 5% concentration of a salt and which decreases the solubility of said solvent in said non-solvent, and subjecting the materials to a stretching operation.

14. Process for the manufacture of artificial filaments, threads, yarns, ribbons and like materials, which comprises extruding a solution having a basis of organic derivatives of cellulose into an aqueous coagulating bath containing a solution of a solvent for the cellulose derivative in a non-solvent therefor, subjecting the products issuing from said bath and while they are carrying a solution of said solvent in water to the action of a substantially saturated solution of a salt which decreases the solubility of said solvent in water, and subjecting the materials to a stretching operation.

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