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PRODUCTION OF ARTIFICIAL FILAMENTS,
FILMS, AND LIKE MATERIALS

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This invention relates to the production of artificial products, for example filaments, threads, ribbons, films and the like from solutions of cellulose derivatives, for example cellulose acetate, propionate, butyrate or other esters of cellulose or methyl, ethyl or benzyl cellulose or other cellulose ethers and is a continuation in part of U. S. application S. No. 402,785, filed October 26, 1929.

In U. S. application S. No. 402,785, filed October 26, 1929, we have described processes for the production of strong filaments, films, threads or other products by extruding solutions of cellulose derivatives into suitable coagulating baths and so conducting the process that the materials upon emergence from the bath are in a plastic state, that is to say, in a state in which they do not exhibit elasticity or alternatively they are carried into a secondary bath which produces this plasticity. In effect this is brought about by having the filaments or other products in contact at some stage of their production with solutions of solvents for the cellulose derivative of high concentration. In the said U. S. application three methods are described for achieving this object, namely (1) by incorporating in the spinning solutions solvents of higher boiling point than the non-solvent to be employed in the coagulating bath, (2) by incorporating solvents or swelling agents in the coagulating bath itself in high concentration, and (3) by passing the formed products from a coagulating bath into a subsequent treatment bath containing the solvents. If desired any two or more of these three methods may be combined to produce their cumulative effect. Preferably the solvents used are such that by reason of their innocuous properties they need not be washed out of the materials, and a small proportion thereof may be allowed to dry in. Moreover the solvents used are preferably relatively non-volatile or at least less volatile than the non-solvent medium, e. g. water, methyl alcohol or other alcohols employed in the subsequent treatment bath. The solvents employed may, for example, be diacetone alcohol, diethyl tartrate, mono- or diacetyl, ethyl lactate, dioxane or lactic acid.

In a further U. S. application S. No. 437,423, filed March 20, 1930, we have described the advantages of conducting any of the wet spinning operations referred to above so that the coagulating bath or subsequent treatment bath is main-

tained at a temperature above atmospheric or so that the drying of the filaments, threads or other products after emergence from the coagulating bath or subsequent treatment bath is conducted under controlled conditions, for example in a controlled current of air or other drying medium, such control being preferably effected by passing the filaments and the like after emergence from the bath through a cell or chamber similar to that used in the dry spinning art.

The present invention relates to improvements in all such processes of wet spinning artificial products. The new process is of particular value in the case of precipitating baths or subsequent treatment baths which contain the solvent in a relatively high proportion.

According to the present invention while effecting coagulation of the filaments or other products from solutions of cellulose derivatives under such conditions that they are subjected to a strong solvent action, or while treating the filaments or other products immediately subsequent to their production with strong solutions of solvents, salts, sugars or other polyhydric alcohols or other substances capable of reducing the solubility of the solvent in the non-solvent medium are present. The invention is of particular importance when the non-solvent medium employed in the coagulating bath or in the subsequent treatment bath is water, and in effect the addition of the salts, sugars and other substances increases the osmotic pressure of the bath.

The new invention may be carried into effect in a number of ways. For example solutions of cellulose derivatives may be extruded into a coagulating bath consisting of a strong solution of a solvent for the cellulose derivative and containing the salts, sugars or other substances referred to. Or again a solution of a cellulose derivative containing a solvent of higher boiling point than the non-solvent medium to be employed in the coagulating bath may be extruded into water or other non-solvent medium containing the salts or other substances. As a further modification filaments, threads, films or other products formed by coagulation in a suitable coagulating bath or formed by a dry spinning process may be carried directly into a subsequent treatment bath consisting of a strong solution of a solvent and containing salts, sugars or other added substances.

The salts or substances which either prevent the delustering action of hot or boiling aqueous media or which are capable of restoring or imparting lustre to partially delustered products are particularly valuable, see U. S. Patent Nos. 1,765,581 and 1,774,184.

The salts which are particularly suitable for the purpose of the present invention are salts which are insoluble in the solvent employed either in the spinning solution, in the coagulating bath or in the subsequent treatment bath and which are not hydrolysed by the water in the coagulating bath or subsequent treatment bath. In general therefore normal salts are employed which are compounds of strong bases with strong acids. The salts may be employed in any suitable concentration short of the concentration necessary to cause a separation of the solvent from the non-solvent medium in the coagulating bath or subsequent treatment bath. In general therefore only comparatively low concentrations of salts are possible. For example in a 50% aqueous diacetone alcohol solution or aqueous ethyl lactate solution most salts are only soluble to a maximum extent of about 10%, and in fact with percentages up to 10 very valuable results are obtained. Higher percentages may be employed if stable spinning is possible, but 15 to 20% represents about the maximum which may be used consistent with the presence, at some stage of the coagulation or subsequent treatment, of solvents in high concentration. As examples of suitable salts for use according to the present invention the following may be instanced:—sodium sulphate, sodium chloride, sodium acetate, sodium nitrate and sodium phosphate, ammonium sulphate, ammonium chloride and 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 sulphate, ammonium chloride, ammonium nitrate and potassium acetate in proportions of 1, 2, 5 or 8 up to 10% on the weight of the bath. The salts used for the purpose of the present invention have little or no swelling action upon the cellulose derivative. A further class of bodies for use according to the present invention consists, as already indicated, in sugars and other polyhydric alcohols, for instance glucose, fructose, sucrose, xylose, mannitol, sorbitol, cellulose, γ -cellulose or other soluble degradation or depolymerisation products of cellulose.

As with the salts referred to above the sugars and other polyhydric alcohols may be used in coagulating baths or in subsequent treatment baths in any concentration up to the point at which they would cause a separation of the solvent from the non-solvent medium employed therein. For instance when using a coagulating bath or subsequent treatment bath of aqueous diacetone alcohol in a 50–55% concentration an addition of about 20% of glucose will usually cause separation. Such a concentration of glucose is too high for this particular bath. The quantity of sugar or other polyhydric alcohol capable of causing separation of the bath into two layers will naturally vary with the particular solvent employed in the bath, with the non-solvent employed therein and with the relative proportions. In no case however should the sugars and like substances be used in a concentration in excess of 30% of the weight of the bath, since higher concentrations unduly increase the vis-

cosity of the bath and render spinning difficult. Concentrations of 5, 10, 15 or 20% of glucose or like sugars yield very valuable results in the present processes.

It therefore appears that concentrations of salts of about 15–20% on the weight of the bath and concentrations of sugars of about 30% on the weight of the bath represent the outside limits for producing the valuable results of the present processes.

It has further been found that the use of the sugars or other polyhydric alcohols as described above reduces or eliminates any tendency that the filaments or other products may have of sticking together after spinning, owing perhaps to local accumulation of the solvent on the yarn.

The sugars, salts or other agents capable of exerting an osmotic pressure or capable of reducing the solubility of the solvent in the non-solvent employed in the coagulating or subsequent treatment bath may be employed in conjunction with any of the processes described in U. S. applications S. Nos. 402,785 filed October 26, 1929 and 437,423 filed March 20, 1930. As described in these U. S. applications by varying the concentrations of solvent employed either in the coagulating bath or in the subsequent treatment bath or in the spinning solution products having almost any degree of lustre may be produced, for example from a very high lustre down to a medium lustre or a relatively low lustre, such as that of natural silk, or having an almost mat or non-lustrous appearance. Again the concentration of salt, sugar or like substance employed also determines to some extent the lustre of the products produced, the lustre in general increasing with the concentration of salt, sugar or other added substance in the bath.

The solvents may be removed from the yarn or other products by simple washing or by any other suitable process, and reference is made broadly to the description in U. S. application S. No. 402,785 filed October 26, 1929 for such treatments. The filaments, threads or the like may be wound in any suitable manner, as for example on bobbins or in a centrifugal spinning box or they may be dried and twisted and wound, as for example on cap spinning devices as described in U. S. application S. No. 437,423 filed March 20, 1930.

Products of relatively high lustre produced according to the invention are delusterable or partially delusterable by means of hot or boiling water or aqueous liquors or by means of moist steam. The lustre of products so delustered may however be restored by treatment with salts or solvents as described in U. S. Patent Nos. 1,774,184 and 1,808,098. By means of boiling aqueous liquors applied without tension products are obtainable having a very pleasing pearly lustre and a soft handle. As opposed to the above products, products having a relatively low lustre obtainable by the present invention do not appear to be affected by any of the above agencies. The directly spun products or the delustered or re-lustered products obtained therefrom may be utilized in a variety of ways to obtain differential lustre effects. For example a cellulose acetate yarn of relatively low lustre may be woven, knitted or otherwise made up with the cellulose acetate yarn of relatively high lustre obtainable by the present process or by any other process, for instance the ordinary dry spinning process, to give a product showing a differential lustre. On subjecting such a product to a delustering

agent the highly lustrous portion may be caused to lose its lustre wholly or in part and the portion of low lustre may remain substantially unaffected.

- 5 The following examples show the best methods known to us for carrying the invention into effect, but they are not to be considered as limiting the invention in any way:—

Example 1

- 10 A 25% solution of cellulose acetate in acetone is spun through a jet having orifices of .08 millimetre diameter into a spinning bath consisting of:—

	Parts by weight
15 Diacetone alcohol.....	45
Sodium acetate.....	8
Water.....	47

- 20 The filaments are carried round a feed roller rotating at a peripheral speed of say 25 to 50 or even up to 100 metres per minute, and the filaments are thereafter washed with water and wound on bobbins or collected in a centrifugal spinning box as required. Low filament deniers of 1.0 or less may thus be produced.

Example 2

- 30 The process is carried out as in Example 1 with the exception that the coagulating bath has the following composition:—

	Parts by weight
Ethyl lactate.....	49
Sodium chloride.....	2
Water.....	49

- 35 The product has a somewhat lower lustre than that produced according to Example 1.

Example 3

- 40 A 25% solution of cellulose acetate in acetone containing ethyl lactate equivalent to 25% on the weight of the cellulose acetate is spun into a bath consisting of an aqueous solution of 10% of ethyl lactate and 15% of ammonium sulphate, the filaments being carried over a feed roller rotating at a peripheral speed of 25 to 40 metres per minute and thereafter being collected by any desired method.

Example 4

- 50 A 25% solution of cellulose acetate in acetone is spun into a coagulating bath consisting of:—

	Parts by weight
50 Diacetone alcohol.....	50-55
55 Glucose.....	12½- 7½
Water.....	37½

The spinning, washing and collecting is effected as before.

Example 5

- 60 A 25% solution of cellulose acetate in acetone is spun into a bath containing:—

	Parts by weight
Ethyl lactate.....	50
65 Glucose.....	5
Water.....	45

The lustre of the products is rather less than that obtained according to Example 1.

Example 6

- 70 A 25% solution of cellulose acetate in acetone is spun into a coagulating bath consisting of:—

	Parts by weight
75 Diacetone alcohol.....	25
Water.....	75

The thread is carried round a feed roller rotating at a peripheral speed of 40-50 metres per minute and is thence carried directly to a secondary bath consisting of:—

	Percent by weight
5 Diacetone alcohol or ethyl lactate.....	50
Glucose.....	10
Or sodium acetate or chloride.....	2- 6

and the remainder water. The thread is thereafter washed and reeled as desired.

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

1. Process for the production of artificial filaments and threads, which comprises extruding a solution of cellulose acetate in a neutral solvent medium through a shaping device into an aqueous coagulating medium having a strong plasticizing action on the shaped material so that they emerge therefrom in a highly plastic state, said medium containing ethyl lactate in a concentration of between 45-55% and a low concentration of an inorganic salt which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

2. Process for the production of artificial filaments and threads, which comprises extruding a solution of cellulose acetate in a neutral solvent medium through a shaping device into an aqueous coagulating medium having a strong plasticizing action on the shaped materials so that they emerge therefrom in a highly plastic state, said medium comprising diacetone alcohol in a concentration of between 45-55% and a low concentration of an inorganic salt which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

3. Process for the production of artificial filaments and threads, which comprises extruding a solution of cellulose acetate in a neutral solvent medium through a shaping device into an aqueous medium having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said medium containing between 45 and 55% of diacetone alcohol and between 1 and 5% of a salt selected from the group consisting of sodium chloride and sodium acetate, and subjecting the materials to a stretching operation while they are in said highly plastic state.

4. Process for the production of artificial filaments and threads, which comprises extruding a solution of cellulose acetate in a neutral solvent medium through a shaping device into an aqueous medium having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said medium containing between 45 and 55% of ethyl lactate and between 1 and 5% of a salt selected from the group consisting of sodium chloride and sodium acetate, and subjecting the materials to a stretching operation while they are in said highly plastic state.

5. In the production of artificial filaments, threads, ribbons, films, and similar products from solutions of organic derivatives of cellulose in neutral solvent media by wet spinning processes, the step of subjecting the shaped material to the action of a liquid bath having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said bath comprising a non-solvent for the cellulose derivative, between 25 and 65% of a less volatile neutral solvent for the cellulose derivative, said non-sol-

vent and solvent being miscible, and a low concentration of a substance which reduces the solubility of the solvent in the non-solvent.

6. In the production of artificial filaments, threads, ribbons, films, and similar products from solutions of organic derivatives of cellulose in neutral solvent media by wet spinning processes, the step of subjecting the shaped material to the action of an aqueous bath having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said bath comprising a neutral solvent for the cellulose derivative which is less volatile than and miscible with water and which is present in a concentration of between 25 and 65%, and a low concentration of a substance which reduces the solubility of the neutral solvent in water.

7. In the production of artificial filaments and threads from solutions of organic derivatives of cellulose in neutral solvent media by wet spinning processes, the step of subjecting the shaped material to the action of an aqueous medium having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said medium comprising a neutral solvent for the cellulose derivative which is less volatile than and miscible with water and which is present in a concentration of between 25 and 65%, and a low concentration of a substance which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

8. Process for the production of artificial filaments, threads, ribbons, films and similar products, which comprises extruding a solution of an organic derivative of cellulose in a neutral solvent medium through a shaping device into a liquid coagulating bath having a strong plasticizing action on the shaped material so that they emerge therefrom in a highly plastic state, said bath comprising a non-solvent for the cellulose derivative, between 25 and 65% of a less volatile neutral solvent for the cellulose derivative, said solvent and non-solvent being miscible, and a low concentration of a substance which reduces the solubility of the solvent in a non-solvent, and stretching the materials while they are in said highly plastic state.

9. Process for the production of artificial filaments, threads, ribbons, films and similar products, which comprises extruding a solution of an organic derivative of cellulose in a neutral solvent medium through a shaping device into an aqueous coagulating bath having a strong plasticizing action on the shaped material so that they emerge therefrom in a highly plastic state, said medium comprising a neutral solvent for the cellulose derivative which is less volatile than and miscible with water and which is present in a concentration of between 25 and 65%, and a low concentration of a substance which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

10. Process for the production of artificial filaments and threads, which comprises extruding a solution of an organic derivative of cellulose in a neutral solvent medium through a shaping device into an aqueous coagulating medium having a strong plasticizing action on the shaped materials so that they emerge therefrom in a

highly plastic state, said medium comprising a neutral solvent for the cellulose derivative which is less volatile than and miscible with water and which is present in a concentration of between 25 and 65% and a low concentration of an inorganic salt which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

11. Process for the production of artificial filaments, threads, ribbons, films and similar products, which comprises extruding a solution of an organic derivative of cellulose in a neutral solvent medium through a shaping device into an aqueous coagulating medium having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said medium comprising a neutral solvent for the cellulose derivative which is less volatile than and miscible with water and which is present in a concentration of between 25 and 65% and between 1 and 10% of an inorganic salt which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

12. Process for the production of artificial filaments and threads, which comprises extruding a solution of cellulose acetate in a neutral solvent medium through a shaping device into an aqueous medium having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said medium comprising a relatively non-volatile neutral solvent for the cellulose acetate in a concentration of between 45 and 55%, said solvent being miscible with water, and between 1 and 5% of an inorganic salt which reduces the solubility of the solvent in water, and subjecting the materials to a stretching operation while they are in said highly plastic state.

13. Process for the production of artificial filaments and threads, which comprises extruding a solution of cellulose acetate in a neutral solvent medium through a shaping device into an aqueous medium having a strong plasticizing action on the materials so that they emerge therefrom in a highly plastic state, said medium containing a relatively non-volatile neutral solvent for cellulose acetate in concentration of between 25 and 65%, said solvent being miscible with water, and between 1 and 10% of a salt selected from the group consisting of sodium chloride and sodium acetate, and subjecting the materials to a stretching operation while they are in said highly plastic state.

14. Process for the production of artificial filaments, threads, ribbons, films and similar products, which comprises extruding a solution of the cellulose derivative in a neutral solvent medium through a shaping device into an aqueous coagulating medium having a strong plasticizing action on the shaped materials so that they emerge therefrom in a highly plastic state, said medium containing a non-solvent selected from the group consisting of ethyl lactate and diacetone alcohol in a concentration of between 45 and 55%, and between 1 and 10% of an inorganic salt which reduces the solubility of the solvent in water, and stretching the materials while they are in said highly plastic state.

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