

UNITED STATES PATENT OFFICE

2,039,307

MANUFACTURE OF ARTIFICIAL FILAMENTS,
THREADS, RIBBONS, FILMS, AND OTHER
ARTIFICIAL PRODUCTS

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No Drawing. Application July 13, 1933, Serial
No. 680,253. In Great Britain July 14, 1932

7 Claims. (Cl. 106—40)

This application is a continuation in part of my application S. No. 495,138 filed 12th November, 1930 and relates to the manufacture of artificial filaments, threads, yarns, ribbons, films and the like and to fabrics and similar materials made from or containing such products, and more particularly to the manufacture of such products having a reduced, subdued or modified lustre.

which has been dissolved in sulphuric acid, zinc chloride, thiocyanates, Schweitzer's reagent or other solvents may be precipitated from its solution by suitable means. Again, cellulose may be precipitated from a viscose solution and cellulose derivatives such as cellulose esters and ethers, e. g. cellulose acetate, cellulose formate, cellulose propionate, cellulose butyrate, cellulose benzoate, methyl, ethyl and benzyl cellulose, may be precipitated from their solutions in suitable solvents.

Precipitating agents may be used which cause precipitation by virtue of their diluent action on the solvent, or which react with the solvent.

I have further discovered that cellulose benzoates, particularly dibenzoyl cellulose, prepared in a finely divided condition, are of considerable value in delustring artificial textile materials of the cellulosic type such as viscose, nitrocellulose, or cuprammonium silks, and also textile materials made of certain cellulose derivatives with which they are incompatible or incompletely compatible, e. g. acetone-soluble cellulose acetate, ethyl cellulose acetate, and oxyethyl cellulose acetate. The dibenzoyl cellulose or other cellulose benzoate may be prepared in a finely divided condition by any suitable means, e. g. by grinding, or atomizing from solution or by any other of the methods described in application S. No. 495,138, or may very advantageously be prepared in a finely divided state by precipitation from solution in accordance with the processes described in this application.

I prefer to carry out the precipitation by treating the solution of the fibrous material with precipitating agents, at normal or elevated temperatures, though in some cases a heat treatment may itself be sufficient to cause precipitation. Cellulose may be precipitated from its solution in mineral acids, such as sulphuric acid, hydrochloric acid, or mixed acids, by means of water or solutions of salts such as alkali chlorides or sulphates. It is preferable to carry out this process on freshly prepared solutions, and it is also preferable to prepare such solutions at low temperature in order to avoid undue degradation of the cellulose molecule. Solutions of cellulose in zinc chloride may also be precipitated by water, dilute acids or other diluents, for example alcohol. If the precipitate obtained from zinc chloride solutions contains zinc compounds they may be removed by treatment with suitable dilute acids. Cuprammonium solutions of cellulose may be treated with salts, acids, alkalies and other substances, for example sugar, to precipitate the

My application S. No. 495,138 describes processes wherein finely divided fibrous materials are incorporated in the spinning solutions, such fibrous material being insoluble in the spinning solution to which it is added. The fibrous material is, therefore, of a different nature from the base of the spinning solution. Any type of organic fibrous material may be employed. Such materials may be natural materials, as for example cotton, linen, straw and other vegetable cellulosic materials, silk, wool and other animal fibres, or artificial materials such as regenerated cellulose or cellulose derivative fibres. The fibrous materials should be incorporated in the spinning solution in a very fine state of subdivision. Several processes are described for obtaining the fibrous materials in a finely divided form; for example the organic fibrous material may be ground in a suitable mill with or without the admixture of small or large quantities of suitable liquids, e. g. water, acetone or other liquids, used for dissolving the viscose, cellulose acetate or other base. The organic fibrous material may moreover be ground in admixture with the base and in the presence or absence of suitable liquids. In this last process the product is dissolved in a suitable solvent and the solution so obtained contains the organic fibrous material in a finely divided form. Again, the organic fibrous materials may be reduced to a fine state by atomizing their solutions into a suitable drying or coagulating medium; for example a solution of viscose may be atomized into a hot atmosphere preferably containing a coagulating agent such as gaseous hydrochloric acid, or a solution of a cellulose derivative in a volatile solvent may be atomized into an evaporative atmosphere.

I have now discovered that particularly good results may be obtained in the above processes by using organic fibrous material which has been prepared in a very fine state of sub-division by precipitation from solution. The organic fibrous material may be of any kind, either natural or artificial and it may be dissolved in any suitable solvent. Thus, for example, cellulosic material

cellulose, and any copper compounds contained in the precipitated cellulose may afterwards be removed by suitable reagents. Cellulose may be precipitated from viscose solution by the action of acid reagents, and cellulose derivatives may be precipitated from their solutions by the incorporation therewith of non-solvents for the cellulose derivatives. Thus, for example, a solution of dibenzoyl cellulose in an organic solvent may be precipitated in a fine state of sub-division by addition of a suitable non-solvent diluent, for example a hydrocarbon or an ether.

Where the cellulose or cellulose derivative is to be precipitated by means of a liquid agent, I have found that good results may be obtained by agitating or stirring the precipitating liquid. Agitation may be achieved by means of a nozzle delivering the solution of cellulose or cellulose derivative, or stirring or agitating means may be disposed in the precipitating liquid. In addition the solution of the cellulose or cellulose derivative and also the precipitant may be heated, if desired, in any suitable manner as for example by means of a water or steam jacket or by direct heating. Alternatively, the precipitating agent may be squirted through a nozzle situated under the solution under similar conditions. Furthermore the cellulosic material may be precipitated by gaseous means. Thus, cellulose may be precipitated from its cuprammonium solution by means of hydrochloric acid gas, or carbon dioxide, by forcing the precipitating gas through a spraying nozzle into the cellulosic liquid. In this case the movement of the gas may itself give sufficient stirring motion to the solution, or the solution may be further agitated by mechanical means.

Solutions of cellulose derivatives in organic solvents may be treated with non-solvents to precipitate the cellulose derivative in a finely divided form. In this case it may be sufficient merely to incorporate the non-solvent with the either hot or cold cellulose derivative solution whilst stirring, without the aid of squirting nozzles or other similar apparatus. Vigorous agitation will result in the precipitation of the cellulose derivative in a finely divided form. Advantageously the solution of the cellulose derivative in an organic solvent, which solution may be that in which the cellulose derivative has been prepared or may be any other suitable solution, may be brought to a point just short of precipitation by means of a suitable amount of precipitating medium and then incorporated with a further quantity of precipitating medium. Thus for example cellulose may be esterified with acetic anhydride and acetic acid in the usual manner, the esterification solution brought to a point just short of precipitation with dilute acetic acid and the so-treated esterification solution precipitated with a large bulk of water or dilute acetic acid. The physical condition in which the materials are precipitated may to some extent be controlled by the degree of agitation employed and, in general, more vigorous agitation will result in the precipitation of the cellulose derivative in a more finely divided form.

Where cellulosic material is precipitated from its solution by means of diluents or other precipitating media the operation may be carried out in the presence of agents calculated to inhibit agglomeration of the precipitated particles, e. g. mild dispersing agents or protective colloids. Thus for example the precipitation may be carried out in the presence of organic sulphonic

acids or gelatin, glue and the like. In general, however, it is preferable only to employ small quantities of such agents.

The precipitated cellulosic material may be freed from the solvent and precipitation liquors by filtration or ultra-filtration, or may be subjected to dialysis so that the precipitation and solvent liquors are replaced by water. The water may then be replaced, if desired, with acetone or other suitable organic solvent or the aqueous suspension may be employed directly in making up spinning solutions.

In another form of the invention cellulose or a cellulose derivative may be precipitated actually in the spinning solution. Thus for example a solution of cellulose acetate in an organic solvent may be incorporated with a viscose spinning solution so as to precipitate the cellulose acetate throughout the mass in a finely divided condition.

Spinning solutions containing the finely divided fibrous materials prepared according to the present invention may be spun by any suitable process, for example the processes described in application S. No. 495,138 already referred to, according to the nature of the spinning solution employed. Thus, a viscose solution containing a finely divided cellulose derivative in suspension may be extruded into coagulating baths containing dilute or strong mineral acids or organo-mineral acids, or containing salts or acid salts, with or without the addition of other substances, and a solution containing cellulose acetate or other cellulose derivatives and finely divided cellulose in suspension may be dry or wet spun into suitable evaporative or coagulative media.

The following examples are given in order to illustrate the invention but are not to be considered as limiting it in any way:—

Example 1

10 parts of cellulose, for example in the form of purified wood pulp, are dissolved in 50-60 parts of strong sulphuric acid. The solution is preferably prepared at low temperatures, e. g. at temperatures of 0-10° C., in order to reduce degradation of the cellulose molecule. The solution is diluted with water to a point just short of that at which precipitation would occur and is then injected as a fine spray into a concentrated solution of sodium sulphate, the solution being vigorously agitated during the addition. The suspension of finely divided cellulose in the precipitating medium thus obtained may be transferred to a dialyzer and freed from sodium sulphate and sulphuric acid by means of water. The fine aqueous suspension is centrifuged in order to concentrate the precipitate as much as possible and the water of the resulting suspension is replaced by acetone by any convenient method, as for example by successively diluting the suspension with acetone and centrifuging. The acetone suspension is then employed in preparing a 25% solution of cellulose acetate in acetone, and the proportion of cellulose thus incorporated in the spinning solution is adjusted to be about 3-5% calculated on the weight of the cellulose acetate. This spinning solution is spun in any suitable manner either by dry or wet spinning methods and the filaments produced possess a subdued lustre.

Example 2

A 10% solution of dibenzoyl cellulose in chloroform is sprayed into an excess of alcohol, the operation being carried out with vigorous stirring.

ring of the precipitating liquor. The dibenzoyl cellulose is thus precipitated in a finely divided form and is separated from the bulk of the liquors by centrifuging. The finely divided dibenzoyl cellulose is incorporated into a viscose spinning solution to the extent of about 3% calculated on the base of the viscose solution. Filaments prepared from this solution possess a subdued lustre.

10 The term "cellulosic material" in this specification, unless the context otherwise requires, and in the claims, is to be construed as covering not only cellulose itself but conversion products thereof such as oxycellulose and hydrocellulose and derivatives of cellulose, such as viscose, and cellulose esters or ethers.

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

20 1. Artificial filaments, threads, ribbons, films and the like having a basis of cellulosic material incompatible with cellulose benzoate and containing finely divided cellulose benzoate.

25 2. Artificial filaments, threads, ribbons, films and the like having a basis of cellulosic material incompatible with dibenzoyl cellulose, and containing finely divided dibenzoyl cellulose.

3. Artificial filaments, threads, ribbons, films and the like having a basis of an organic derivative of cellulose incompatible with dibenzoyl cel-

lulose and containing finely divided dibenzoyl cellulose.

4. Artificial filaments, threads, ribbons, films and the like having a basis of cellulose acetate incompatible with dibenzoyl cellulose and containing finely divided dibenzoyl cellulose. 5

5. A spinning solution for use in the manufacture of artificial filaments, threads, and the like which comprises a cellulosic material dissolved in a suitable solvent therefor and which contains, as a disperse phase, a finely divided cellulose benzoate which is incompatible with the said cellulosic material. 10

6. A spinning solution for use in the manufacture of artificial filaments, threads, and the like which comprises an organic derivative of cellulose dissolved in a suitable solvent therefor and which contains, as a disperse phase, a finely divided dibenzoyl cellulose which is incompatible with the said organic derivative of cellulose. 15 20

7. A spinning solution for use in the manufacture of artificial filaments, threads, and the like which comprises cellulose acetate dissolved in a suitable solvent therefor and which contains, as a disperse phase, finely divided dibenzoyl cellulose which has been obtained in a finely divided form by precipitation from solution. 25

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