Patented Oct. 20, 1936 2,057,712

UNITED STATES PATENT OFFICE

2,057,712

PRODUCTION OF FILAMENTS AND THE LIKE

Henry Dreyfus, London, England

No Drawing. Application August 22, 1932, Serial No. 629,903. In Great Britain September 16, 1931

16 Claims. (Cl. 18—54)

This invention relates to the manufacture of artificial filaments, threads, yarns, ribbons, films or the like of reduced, subdued or modified lustre, and is especially valuable for the production of such materials having a basis of cellulose acetate or other cellulose esters or ethers. The invention also includes fibres or other materials made from or containing such products.

The manufacture of artificial filaments and like products having subdued lustre has recently become of great importance. In most cases the subduing of the lustre has been achieved by incorporating in the spinning solutions used in the manufacture of the materials finely divided powders, and particularly finely powdered pigments, which are worked up with the solvent or with part of the spinning solution before being incorporated in the main bulk of the spinning solution. While the incorporation of these powders, and especially pigments, in the materials leaves little to be desired in the matter of lustre, nevertheless the artificial filaments and other products containing such bodies have disadvantages, the most notable being that they tend to cut the guides which are used either on the spinning machine itself or in the textile processing of the filaments up to the time when they are woven or knitted into fabrics.

I have now found that the required subduing of the lustre can be produced quite efficiently, and at the same time the materials of low lustre have less tendency to cut the guides, by the use of substances which in the solid state are colloidal in character. According to the invention such substances are incorporated in the spinning solutions in suitable proportions for securing the desired degree of delustring, the spinning solutions being then spun by dry or wet spinning methods.

The substances which are to be used in accordance with the present invention are in general those which are precipitated from aqueous media in a gelatinous or flocculent form, and the term "colloidal" is used in this specification in this sense, and not as connoting a particular particle size in the spinning solution. Examples of suitable substances are precipitated oxides, hydroxides or hydrated oxides of titanium, aluminium, zinc and tin. The hydrated oxides used may be those which are termed, for example, ortho- or meta-titanic acids and meta-stannic acid. Other suitable colloidal substances are for example the basic zinc carbonates, and the phosphates, silicates, tungstates, borates, silico-tungstates, tungsto-borates and phospho-tungstates which are insoluble in water, and notably those of the alkaline earth metals, for example calcium, barium or magnesium, and also of aluminium, zinc, tin, lead and titanium.

The colloidal bodies may be reduced to the necessary finely divided state for passage through the spinning nozzles and may be incorporated in the spinning solutions by any suitable methods. I prefer to employ the compounds in the form in which they are precipitated from aqueous solutions of soluble salts or compounds. In this form they exist as gelatinous or flocculent masses permeated with a large mass of water. In order to incorporate them in the spinning solution, these aqueous jellies may, for example, be worked with acetone or other suitable solvent used for making up the spinning solution, or with a small proportion of the spinning solution itself, and the whole then incorporated in the spinning solution, or the aqueous jelly with or without working with acetone or other solvent may be worked with the cellulose acetate or other bases used for manufacturing the spinning solution before the spinning solution is actually made up. If desired, a colloidal solution of the substance may be mixed with a solution of the cellulose acetate or other base, and the whole precipitated to form a convenient "complex" for making up the spinning solution. Such solution may, in the case of organic derivatives of cellulose, be either the esterification or etherification solution itself, or a solution formed by dissolving the cellulose derivative in a suitable solvent.

In most cases it is not necessary to grind the product before incorporating it with the solvent or base of the spinning solution, the necessary subdivision being capable of attainment during the actual process of working. However, if preliminary grinding is resorted to, it is preferable that the solid material should not be dried during any part of this process. It may, for instance, be ground in the presence of the water which is already contained in it or in the presence of excess water. Another method which is suitable for use in accordance with the invention consists in causing the reagents which are adapted to yield the colloidal product to react in the presence of the cellulose acetate or other base used for making up the spinning solution, or in the spinning solution itself. Thus, for example, in the case of employing cellulose acetate as base it is common practice to employ as a solvent an acetone containing 5% or even more of water, and in fact the addition of such water to the spinning solution enables the filaments to be drawn down much more readily to

fine deniers. This added water may be the means of introducing into the spinning solution reagents necessary for the formation therein of the colloidal body. Thus, for instance, cellulose acetate may be dissolved to the desired concentration in anhydrous acetone or acetone containing only little water, one of the reagents dissolved in water added and thoroughly mixed therewith, and then the other reagent also dissolved in water may be added thereto, and the whole mixed thoroughly. In this manner a very uniform incorporation of the colloidal body is achieved. A similar formation of the colloidal body in the presence of the cellulose acetate may be effected by mixing the reagents in the presence of any other suitable solution of the cellulose acetate and subsequently precipitating the "complex" of cellulose acetate and colloidal body. This may then be dissolved in acetone or other desired solvents.

As a further alternative where feasible the reagents necessary for the formation of the colloidal body may be dissolved in organic solvents, and in this form caused to react, for example, in the spinning solution itself, or in the presence of the cellulose acetate or other base. In the case of viscose or like aqueous spinning solutions the formation of the colloidal body in the midst of the spinning solution may take place in a normal manner by reaction of the reagents dissolved in the aqueous reagents.

Either during the working of the colloidal body with the spinning solution or with the constituents thereof, or during a preliminary grinding, the colloidal body is, if necessary, reduced to the required state of sub-division to enable it to pass the spinning nozzles in the spinning of artificial filaments of commercial deniers. It is usually sufficient to attain a particle size of somewhat less than 0.003 mm., but if desired the average particle size may be reduced to 0.0001 to 0.0005 mm.

If desired, together with the colloidal body other reagents, and especially reagents adapted to assist the dispersion of the colloidal body in the spinning solution, may be added, for example Turkey red oil, preferably applied in relatively small proportions, or other oils, as for example oleic acid, linseed oil, olive oil, white petroleum oil and the like.

The following examples illustrate the invention but it is to be understood that they do not limit it in any way.

Example 1

A fairly concentrated solution containing about 210 parts by weight of $Al(NO_3)_3$ is added to a solution of about 130 parts by weight of NaOH, the aqueous suspension of $Al(OH)_3$ heated to boiling for a short time and the precipitate then filtered off and washed free from soluble salts. The mass of aluminium hydroxide is then worked up with acetone and incorporated in a spinning solution of cellulose acetate in acetone, or it may, if desired, be worked up with a portion of the spinning solution or with the cellulose acetate itself.

Example 2

A solution containing about 1% by weight of zinc nitrate is poured at room temperature into an equivalent solution of sodium carbonate also of about 1% concentration with good stirring. The precipitate is well washed with water, and may then be incorporated in a spinning solution as described in Example 1.

As previously indicated, the spinning solutions prepared as described above may be spun by dry or wet spinning processes.

The invention may be applied to the manufacture of dulled filaments or other products from viscose or other aqueous solutions, but is most valuable in its application to the spinning of solutions of cellulose acetate or other cellulose esters or ethers, for example cellulose formate, cellulose propionate, cellulose butyrate, cellulose nitroacetate or other organic esters of cellulose, cellulose nitrate, or cellulose ethers, e. g. ethyl or benzyl cellulose, or mixed ether-esters. Where, in the accompanying description reference is made to substances in a "colloidal form", it is to be understood that the term implies only substances which are in a gelatinous or flocculent form.

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

1. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like having a modified lustre, which comprises forming the said products from spinning solutions containing an insoluble inorganic substance in a gelatinous or flocculent form.

2. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises forming the said products from solutions of cellulose acetate, which solutions contain a substantially white insoluble inorganic substance in a gelatinous or flocculent form.

3. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises incorporating in solutions of cellulose acetate a substantially white insoluble inorganic substance in a gelatinous or flocculent form permeated with water, prepared, prior to its incorporation, by precipitation from aqueous media, and forming the said products from the resulting solutions.

4. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises forming the said products from solutions of cellulose acetate, which solutions contain aluminum hydroxide in a gelatinous or flocculent form permeated with water, the said aluminum hydroxide being formed by precipitation from aqueous media prior to it incorporation into the solutions.

5. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises forming the said products from solutions of cellulose acetate, which solutions contain basic zinc carbonate in a gelatinous or flocculent form permeated with water, and said basic zinc carbonate being formed by precipitation from aqueous media prior to its incorporation into the solutions.

6. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises forming the said products from solutions of cellulose acetate, which solutions contain a tungstate of an alkaline earth metal in a gelatinous or flocculent form permeated with water, the said tungstate of an alkaline earth metal being formed by precipitation from aqueous media prior to its incorporation into the solutions.

7. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises forming the said products from solutions of cellulose acetate, which solutions contain, in a gelatinous or flocculent form, barium tungstate.

8. Process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which comprises forming the said products from solutions of cellulose acetate, which solutions contain barium tungstate in a gelatinous or flocculent form permeated with water, the said tungstate being formed by precipitation from aqueous media prior to its incorporation.

9. Artificial filaments, threads, yarns, ribbons, films and the like having a modified lustre, which contain particles of an inorganic substance in a gelatinous or flocculent form.

10. Artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which contain particles of a substantially white insoluble inorganic substance in a gelatinous or flocculent form.

11. Artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which contain particles of aluminum hydroxide in a gelatinous or flocculent form, the particle size of the aluminum hydroxide being between 0.003 and 0.0005 mm.

12. Artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which contain particles of basic zinc carbonate in a gelatinous or flocculent form, the particle size of the basic zinc carbonate being between 0.0001 and 0.0005 mm.

13. Artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which contain particles of a tungstate of an alkaline earth metal in a gelatinous or flocculent form, the particle size of the tungstate of the akaline earth metal being between 0.003 and 0.0005 mm.

14. Artificial filaments, threads, yarns, ribbons, films and the like containing cellulose acetate and having a modified lustre, which contain particles of barium tungstate in a gelatinous or flocculent form.

15. In a process for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like having a modified lustre, the steps of forming a solution of a suitable base and containing a finely divided insoluble substantially white inorganic substance in a gelatinous or flocculent form distributed throughout the solution and extruding the solution through suitable orifices into a setting medium.

16. Solutions for the manufacture of artificial filaments, threads, yarns, ribbons, films and the like having a modified lustre which comprise a finely divided insoluble inorganic substance in a gelatinous or flocculent form distributed throughout a solution of an organic derivative of cellulose.

HENRY DREYFUS.