Oct. 5, 1937. H. DREYFUS 2,094,781

MANUFACTURE OF ARTIFICIAL FILAMENTS, THREADS, RIBBONS, AND THE LIKE

Filed March 18, 1933

FIG. 1

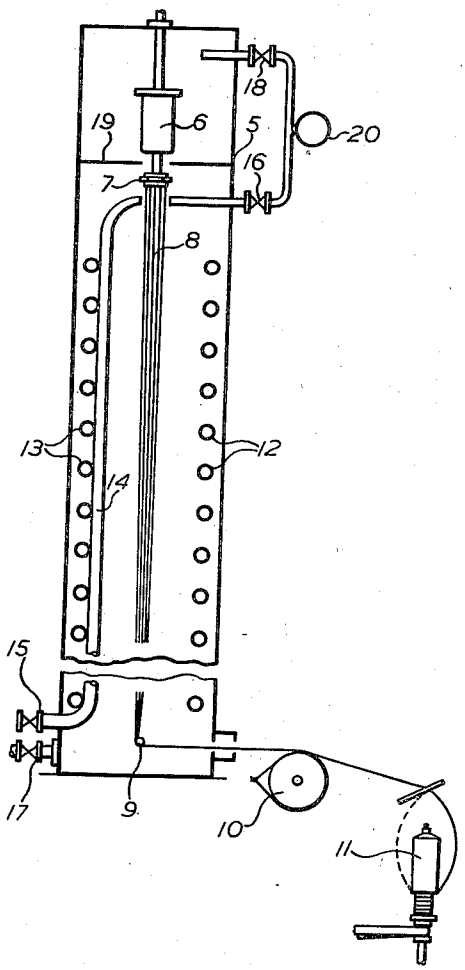


FIG. 2

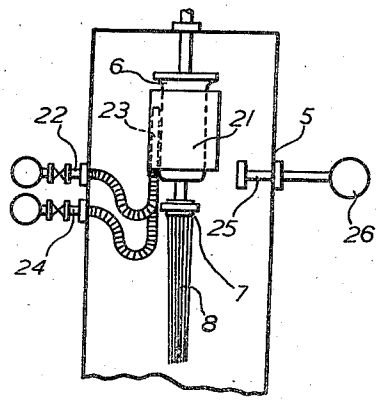
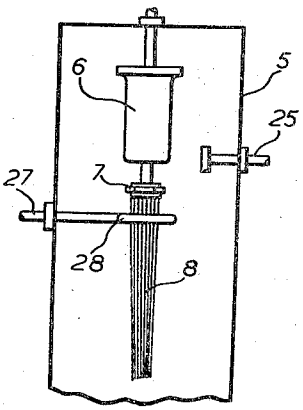


FIG. 3



HENRY DREYFUS
INVENTOR

Selfridge & Robinson
ATTORNEYS

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MANUFACTURE OF ARTIFICIAL FILAMENTS, THREADS, RIBBONS, AND THE LIKE

Henry Dreyfus, London, England

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8 Claims. (Cl. 18—54)

This invention relates to improvements in the manufacture of artificial products, and more particularly to the manufacture of artificial filaments, threads, ribbons and the like from solutions of cellulose derivatives by the dry spinning or evaporative method.

As customarily practised the manufacture of artificial filaments from cellulose acetate by the dry spinning method consists in dissolving the cellulose acetate having a viscosity characteristic of about 6 to 20 or 25 (determined by measuring the rate of flow of a 6% solution of the cellulose acetate in acetone against the rate of flow of glycerine taken as 100) to a concentration of about 15–30% strength, and spinning into an evaporative medium maintained at an appropriate temperature for the evaporation of the solvent within a reasonably short length of travel of the filaments or like products. In these circumstances the products are in general substantially solidified at a distance of 4–6 inches from the jet. Usually the spinning temperature is in the neighbourhood of 65–70° C., the solvent being acetone, though higher temperatures may be used when hollow filaments are to be produced. The spinning solution is itself heated up by the evaporative medium and may without the application of extraneous heating means approach the temperature of the evaporative medium itself.

In U. S. Patent No. 1,708,787 I describe the manufacture of cellulose esters which have high viscosity characteristics, for example a viscosity of 50–100 or even up to 200 or more measured by the above scale. These cellulose esters and similar celluolse esters made by other methods or cellulose ethers having similar characteristics are highly valuable for the manufacture of artificial filaments, threads, and like products by reason of the intrinsic strength of the cellulose ester with consequent high tensile strength in the products. However it is found that the spinning of such cellulose derivatives by normal spinning methods is difficult to achieve by reason of the very high viscosity of the spinning solution. The draw-down of the filaments may be poor and there may be frequent breakages.

The present invention is concerned with the manufacture of artificial filaments and like products from such cellulose derivatives having high viscosity characteristics, i. e. at least 40. The viscosity of a cellulose derivative is in general a measure of its degree of degradation, and is consequently connected with the viscosity of solutions of the cellulose regenerated from such derivative. A convenient manner of comparing the viscosities of such derivatives consists in comparing the viscosities of the cuprammonium solutions of the cellulose regenerated from such derivatives. In order that this may be carried out the regeneration of the cellulose should be effected under conditions such that further degradation of the cellulose does not occur. Thus cellulose esters may be saponified with aniline approximately at its boiling point and the regenerated cellulose may then be dissolved in cuprammonium solution, and the viscosities of the solutions obtained compared. Solutions of the regenerated cellulose obtained from the cellulose derivatives (other than cellulose acetate) employed according to the present invention yield cuprammonium solutions having a viscosity at least that of a cuprammonium solution of equal concentration of the cellulose regenerated from a cellulose acetate having the same content of substituent groups and having a viscosity of at least 40, measured in acetone solution against glycerine as described above.

According to the present invention the spinning of solutions of such cellulose derivatives is facilitated by increasing the fluidity of the artificial materials during the early stages of spinning, e. g. by increasing the fluidity of the spinning solution itself, or by maintainng the fluidity of the solution after extrusion for a longer period than obtains in normal spinning processes. If, for example, the evaporation is retarded during the early stages of spinning, it is found that spinning is facilitated and the draw-down obtainable is much better than when evaporation proceeds according to normal processes.

Such retardation of the evaporation may be effected by restricting the amount of evaporative medium contacting with the filaments or other products in the early stages of the spinning or drying operation or by reducing the temperature of the evaporative medium in the vicinity of the spinning nozzles.

I find, however, that superior results are produced by incorporating in the spinning solution a liquid of lower volatility than the main solvent of the spinning solution or by making up the spinning solution with solvents, mixtures of solvents or solvent mixtures of lower volatility than the usual solvents employed in dry spinning operations. By this means not only may the fluidity of the spinning solution be maintained for a longer period during the drying of the filaments, but in addition it is possible to raise the temperature to which the spinning solution may conveniently be heated so that the spinning solution possesses increased fluidity before as well as

after extrusion from the spinning nozzle. I find that it is especially advantageous to heat the spinning solution to comparatively high temperatures in order to facilitate the spinning of these high viscosity cellulose derivatives.

Suitable additions to the spinning solution comprise solvents or partial solvents for the cellulose derivative of higher boiling point than the main bulk of the solvent in the spinning solution or of higher boiling point than the normal solvents used in the spinning solution. As already indicated the normal boiling point of the solvent or solvent mixture is of the order of 55–65° C. I find that it is advantageous to employ in the spinning solution a solvent or partial solvent or other liquid having a boiling point above 70, and preferably above 85° C. Thus, for instance, I may use for a high viscosity acetone-soluble cellulose acetate a solvent mixture comprising acetone and substantial proportions of ethyl alcohol or containing acetone and the cyclic ether obtainable from ethylene glycol and formaldehyde having a boiling point of about 75° C. It is, however, still more advantageous to employ in the spinning solution higher boiling liquids, such as dioxane, and other ethers of the glycols and substitution products of such bodies, for example mono-, di- and tri-methyl dioxanes, dioxy dioxane, (though this is rather too high boiling in general), or the di-ethers of dioxy dioxanes, and the homologues of the above bodies, for example the ethyl derivatives of dioxane and of dioxy dioxane. Further examples of high boiling bodies are diacetone alcohol, methyl ethyl ketone, butyrone and ethyl lactate. It is preferable that the higher boiling liquid should have at least some solvent power for the cellulose derivative, particularly when its boiling point differs substantially from the boiling point of the main bulk of highly volatile solvent, if such be employed. Thus it is less advantageous to use benzene and other hydrocarbons which are strongly acting precipitants for acetone-soluble cellulose acetate and certain other cellulose derivatives, and therefore tend to yield opaque or precipitated filaments. Instead of employing the higher boiling body in admixture with acetone or like volatile solvent the solvent may consist of one or more higher boiling bodies. Thus, for example, it is advantageous to spin a high viscosity acetone-soluble cellulose acetate in solution in dioxane alone or in other bodies referred to above which are solvents for the cellulose derivative. I prefer in any case that the higher boiling liquids should constitute a substantial proportion of the total liquid present in the spinning solution, for example a proportion of over 40% and better still over 50 or 60%.

The temperature of the spinning solution prior to extrusion is preferably higher than that obtaining in normal practice, though it will be appreciated that the presence of the higher boiling bodies in the spinning solution tends to maintain the fluidity of the solution after extrusion, so that advantages accrue quite apart from increased temperatures of the spinning solution. However, it is advantageous to heat the spinning solution and to heat it to a higher temperature than that obtaining in the evaporative atmosphere into which the solution is spun. I find that substantially improved results are obtained in general with the high viscosity cellulose derivatives used in accordance with the present invention by maintaining the spinning solution prior to extrusion at a temperature above 75° C., and preferably above 85° C., for example at 90–125° C. The spinning solution may be maintained at this temperature by any suitable means. For example the pumps or the filter candle or other means for leading the spinning solution to the spinning nozzle may be immersed in a suitable attemperating means, or alternatively a heating jacket may be placed around the candle or other supply means, or heating elements may even be immersed in the spinning solution. In this connection reference is made broadly to U. S. Patent No. 2,045,326, which describes means for attemperating the spinning solution before extrusion. In order to maintain a difference in temperature between the spinning solution and the evaporative medium in which the solution is spun, it is preferable to insulate the spinning solution completely from the evaporative medium, e. g. as described in U. S. application S. No. 375,151 filed July 1st, 1929. By this means any desired difference in temperature between the spinning solution and the evaporative medium may be maintained. The spinning solution may in fact be heated up to a temperature below but near to the boiling point of the spinning solution under the pressure obtaining in the spinning nozzle.

If desired the rate of evaporation of the solvent from the spinning solution after extrusion from the spinning nozzles may be reduced by injecting cold or relatively cold air into the region of the nozzles as described in U. S. Patent No. 1,934,618. Such injection may take place either from the inside of the spinning nozzle or from the outside. A further means of maintaining a difference in temperature between the evaporative medium and the spinning solution consists in leading a portion of the evaporative medium heated to a higher temperature than the evaporative medium in the vicinity of the nozzle into contact with the filter candle or other means for leading the spinning solution to the nozzles. Methods of effecting this are described in U. S. application S. No. 653,711 filed February 27, 1933, corresponding to British application No. 7420/32 filed 12th March, 1932, and British application No. 9596/32 filed 4th April, 1932. Again, additional evaporative medium may be introduced into the spinning zone from a source external to the cell, as is described in U. S. Patent No. 2,027,450, and such medium may assist in maintaining the temperature in this region below that of the spinning solution itself.

When it is desired to obtain hollow filaments in accordance with the present invention even while maintaining a relatively low temperature of the air in the vicinity of the spinning nozzles, it is sufficient to bring the filaments some time after extrusion from the spinning nozzle to the requisite high temperature for the formation of the spaces inside the filaments. Thus, for example, a suitable bank of steam pipes or other heating means may be disposed at some distance from the spinning nozzle, for example 12 inches, while ensuring that the hot air from the said heating means is not allowed to enter the vicinity of the spinning nozzles or at least is cooled somewhat prior to such entry.

The artificial materials obtained according to the present invention may be subjected to any desired after-treatment in order to improve or modify their properties, for example they may be treated so as to incorporate therein finely divided inorganic or organic substances for weighting, mordanting or delustring purposes.

Again, they may be subjected to a stretching operation in order to increase their tenacity as described, for example, in U. S. Patent No. 1,709,470 and U. S. applications S. Nos. 378,684 filed July 16th, 1929, 573,424 filed November 6th, 1931 and 602,844 filed April 2nd, 1932, or the materials, whether or not they have previously been stretched, may be treated in the form of filaments, threads, yarns, fabrics or other products with shrinking agents in order to improve their extension or for the production of shrinkage effects, e. g., as described in U. S. applications S. Nos. 607,667 filed April 26th, 1932, and 611,240 filed May 13, 1932, and U. S. Patent No. 2,020,303.

Suitable forms of apparatus for increasing the temperature of the spinning solution before extrusion or reducing the rate of evaporation immediately after extrusion are illustrated in the accompanying drawing, but it is to be clearly understood that they are given merely by way of example and that the invention is by no means limited thereto. Such apparatus may be employed in conjunction with normal spinning solutions or with the special spinning solutions containing liquids of relatively low volatility which form an important feature of the present invention.

Figure 1 illustrates an apparatus in which the rate of evaporation after extrusion is reduced by the introduction of an evaporative medium which is at a lower temperature than that of the main evaporative medium in the cell. The apparatus comprises a spinning cell 5 containing a filter candle 6 and a jet 7 from which a bundle of filaments 8 is extruded. The filament bundle passes round a guide 9 at the bottom of the cell, and through a small aperture to a draw roller 10 from which it passes through a guide to a cap-spinning apparatus 11. Heating coils 12 and 13 are provided and in the neighbourhood of the coils 13 there is fitted a conduit 14, the upper open end of which is directed towards the bundle of filaments 8 while the bottom end communicates through a valve 15 with the external atmosphere. On account of the heating effect of the coils 13 a convection current is induced in the conduit 14 so that a current of air drawn from the external atmosphere is directed upon the filaments in the neighbourhood of the jet. The main evaporative medium is introduced through the inlet at the bottom of the cell, which is provided with a valve 17. The evaporative medium introduced through the conduit 14 is withdrawn through a pipe and valve 16 while the remaining evaporative medium is withdrawn through a pipe and valve 18, both of these pipes communicating with a header 20. A baffle 19 is provided to direct the main evaporative atmosphere into the vicinity of the filter candle 6 in order to assist in heating the dope. Control of the quantity and proportions of evaporative medium introduced may be effected by means of the valves 15, 17, 16, and 18.

Figure 2 shows a form of apparatus in which the dope may be heated in the candle to any desired extent prior to extrusion. The apparatus comprises a spinning cell 5 containing a filter candle 6 communicating with a jet 7 from which the bundle of filaments 8 is extruded. The candle 6 is fitted with a casing 21 into which a heating fluid, for example steam or hot water, is introduced through a pipe 22 which extends towards the top of the casing as indicated at 23. The heating fluid is withdrawn through a pipe 24, and by means of a partition in the casing which is positioned between the inlet pipe 23 and the outlet pipe 24 the heating fluid is forced to pass through the whole of the casing before it is withdrawn through the pipe 24. The evaporative medium is withdrawn through a pipe 25 communicating with a header 26.

Figure 3 shows a form of apparatus in which the rate of evaporation immediately after extrusion is reduced by the introduction of additional evaporative medium at a lower temperature than that of the main evaporative medium in the cell. The apparatus comprises a spinning cell 5 containing a filter candle 6 communicating with a jet 7 from which a bundle of filaments 8 is extruded. Additional evaporative medium is introduced through a pipe 27 communicating with a perforated ring 28 which directs the additional evaporative medium onto the filaments. The evaporative medium is withdrawn from the cell through a pipe 25.

While the invention has been described above more particularly in relation to acetone-soluble cellulose acetate of high viscosity characteristics and particularly a viscosity of over 40, for example 50–100 or more, it may be applied to the manufacture of filaments or like products from other cellulose derivatives having similar viscosity characteristics, for instance cellulose formate, propionate, butyrate, nitro-acetate or other esters or mixed esters of cellulose, or ethyl or benzyl cellulose or other ethers or mixed ethers of cellulose and also mixed ether-esters of cellulose, e. g. ethyl cellulose acetate and oxy-ethyl cellulose acetate.

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

Example 1

A 23% solution of a cellulose acetate having a viscosity of about 40 to 50 dissolved in a solvent mixture consisting of 50 parts acetone and 50 parts dioxane, is extruded through orifices having a diameter of .08 mms. into an evaporative atmosphere. The temperature of the dope prior to extrusion is about 65 to 70° C. while the evaporative medium in the vicinity of the jets is at a temperature of from 60 to 65° C. The filaments obtained may be wound or twisted and wound in any suitable manner, for example by means of a cap spinning apparatus.

Example 2

A 20% solution of a cellulose acetate having a viscosity of about 60 dissolved in a solvent mixture consisting of 80% methyl-ethyl-ketone and 20% ethyl lactate is spun into an evaporative medium as in Example 1, but in this case the temperature of the dope is about 90° C. and the temperature of the evaporative medium from 70 to 75° C.

Example 3

A 21–22% solution of a cellulose acetate having a viscosity of from 65 to 75 dissolved in a solvent mixture consisting of 60% ethylene methylene dioxide and 40% dimethyl dioxane is spun as in the preceding examples, the dope temperature being about 80° C. and the temperature of the evaporative medium being from 65 to 70° C.

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

1. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a

solution which contains an organic ester of cellulose of viscosity at least 40 as defined, an organic solvent therefor having a boiling point of at least 55° C. and at least 40% of an organic liquid of lower volatility which has a boiling point above 70° C. and which has a solvent action on the organic ester of cellulose even at ordinary temperatures and heating the spinning solution to a temperature above 75° C. before extrusion.

2. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a solution which contains an organic ester of cellulose of viscosity at least 40 as defined, an organic solvent therefor having a boiling point of at least 55° C. and at least 40% of an organic liquid of lower volatility which has a boiling point above 70° C. and which has a solvent action on the organic ester of cellulose even at ordinary temperatures and controlling the evaporative atmosphere so as to reduce the rate of evaporation in the vicinity of the spinning jet.

3. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a solution which contains cellulose acetate of viscosity at least 40 as defined, an organic solvent therefor having a boiling point of at least 55° C. and at least 40% of an organic liquid of lower volatility which has a boiling point above 70° C. and which has a solvent action on the cellulose acetate even at ordinary temperatures and controlling the evaporative atmosphere so as to reduce the rate of evaporation in the vicinity of the spinning jet.

4. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a solution which contains an organic ester of cellulose of viscosity at least 40 as defined and a liquid medium which is a solvent even at ordinary temperatures for the cellulose ester, said medium comprising at least 40% of an organic solvent for the cellulose ester having a boiling point of at least 85° C. and an organic solvent for the cellulose ester having a boiling point between 55° and 85° C.

5. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporating method a solution which contains cellulose acetate of viscosity at least 40 as defined and a liquid medium which is a solvent even at ordinary temperatures for the cellulose acetate, said medium comprising at least 40% of an organic solvent for the cellulose derivative having a boiling point of at least 85° C. and an organic solvent for the cellulose derivative having a boiling point between 55 and 85° C.

6. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a solution which contains cellulose acetate of viscosity at least 40 as defined and a liquid medium which is a solvent even at ordinary temperatures for the cellulose acetate, said medium comprising at least 60% of an organic solvent for the cellulose derivative having a boiling point of at least 85° C. and an organic solvent for the cellulose derivative having a boiling point between 55 and 85° C.

7. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a solution which contains cellulose acetate of viscosity at least 40 as defined and a liquid medium which is a solvent even at ordinary temperatures for the cellulose acetate, said medium comprising at least 40% of an organic solvent for the cellulose derivative having a boiling point of at least 85° C. and an organic solvent for the cellulose derivative having a boiling point between 55 and 85° C. and heating the spinning solution prior to extrusion to a temperature only slightly below its boiling point under the pressure obtaining in the spinning nozzle.

8. Process for the manufacture of artificial filaments, threads, yarns and the like, which comprises spinning by the evaporative method a solution which contains cellulose acetate of viscosity at least 40 as defined and a liquid medium which is a solvent even at ordinary temperatures for the cellulose acetate, said medium comprising at least 40% of an organic solvent for the cellulose derivative having a boiling point of at least 85° C. and an organic solvent for the cellulose derivative having a boiling point between 55 and 85° C., and controlling the temperature of the evaporative medium so as to reduce the rate of evaporation in the vicinity of the spinning jet.

HENRY DREYFUS.