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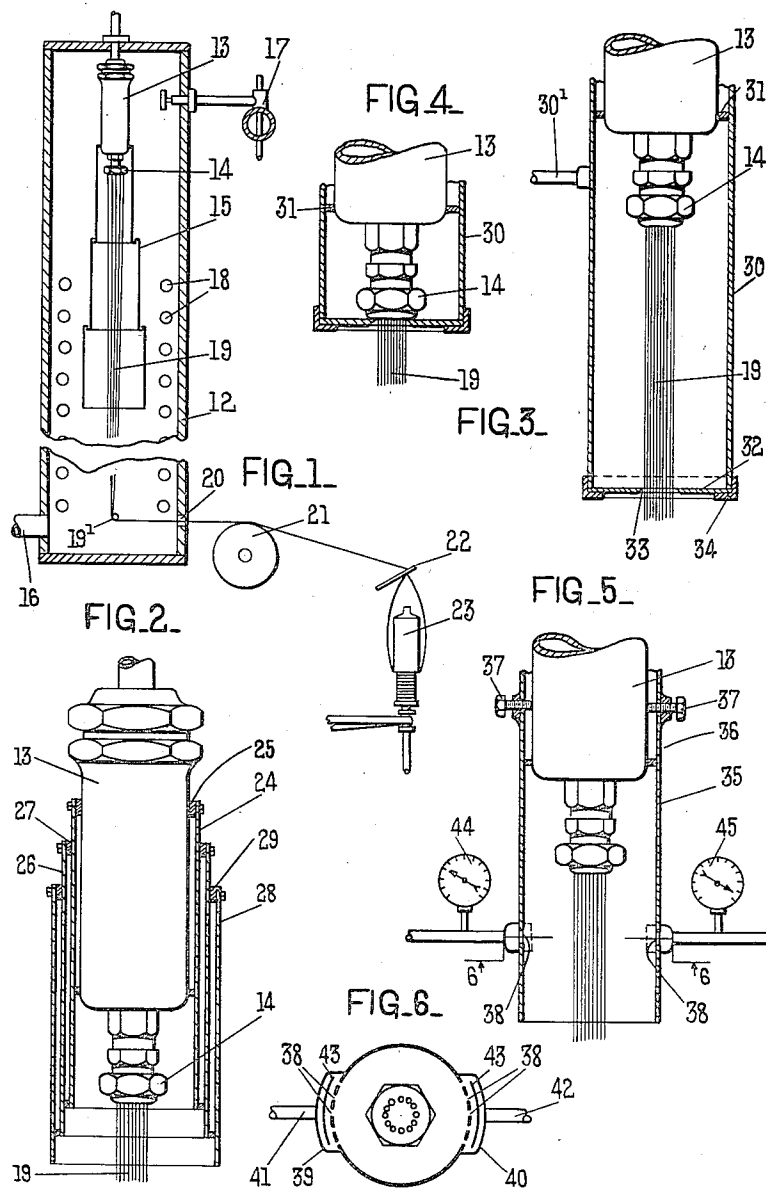
H. DREYFUS ET AL

2,068,538

MANUFACTURE OF FILAMENTS OR THE LIKE OF CELLULOSE DERIVATIVES

Filed Sept. 5, 1931

2 Sheets-Sheet 1



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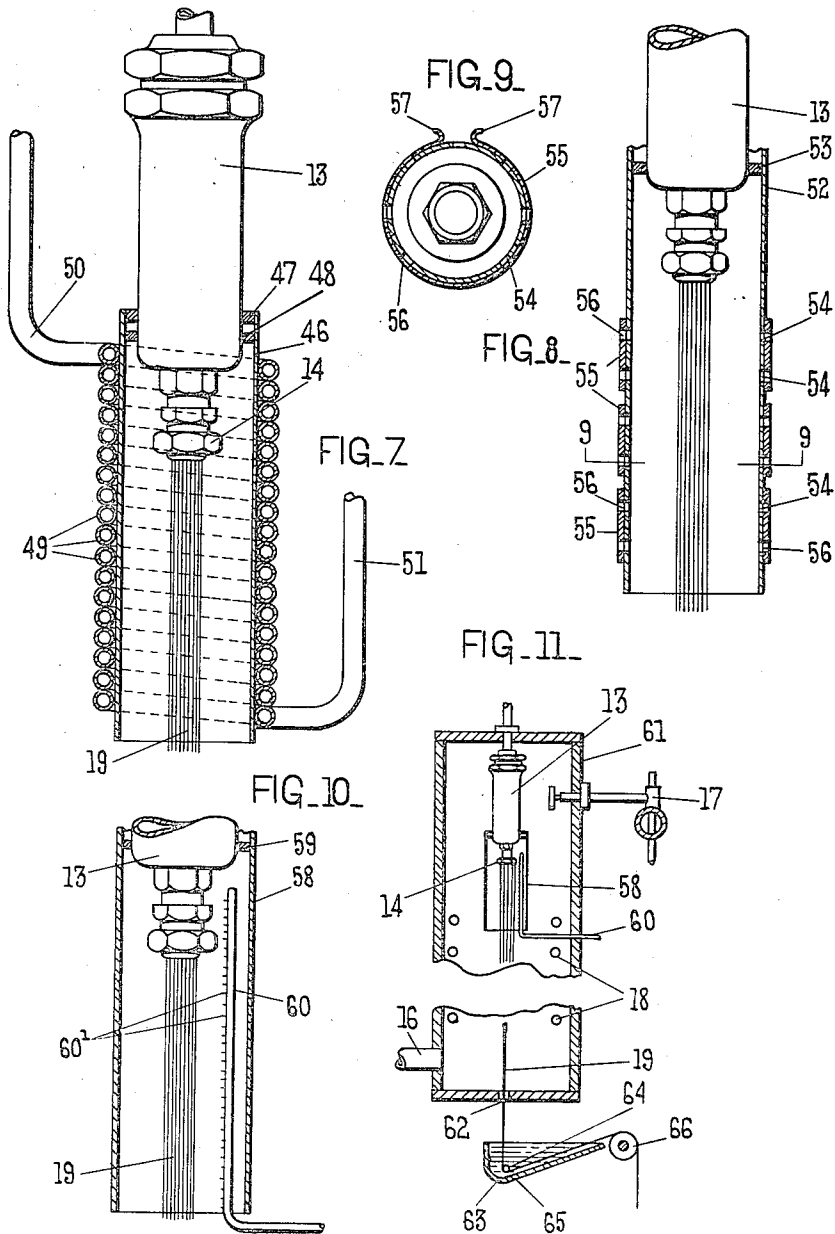
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UNITED STATES PATENT OFFICE

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MANUFACTURE OF FILAMENTS OR THE
LIKE OF CELLULOSE DERIVATIVES

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15 Claims. (Cl. 18—8)

This invention relates to the production of artificial filaments, threads, ribbons, films, and the like from solutions of cellulose acetate or other suitable spinning solutions, for example solutions of other esters of cellulose or of cellulose ethers or other esters.

According to the present invention, spinning solutions, for example solutions of cellulose acetate or other cellulose derivatives are dry spun under such conditions that initially there is little or no evaporation of the solvent, and the more or less liquid filaments or other products are thereafter subjected to processes for evaporating the solvent or for otherwise removing it wholly or in part from the filaments or other products, for example by wet coagulation methods. We have found that by this means products of very low deniers, and at the same time of comparatively high strength, may be obtained. The invention further includes certain modified processes and also new apparatus as hereinafter referred to.

As ordinarily conducted the dry spinning of solutions of cellulose acetate involves an immediate evaporation of the solvent from the filaments or other products. This evaporation is due to the volatility of the solvent used and is customarily accentuated by using a heated spinning solution and/or by spinning into a heated evaporative medium. The evaporation of the solvent may be regulated by a suitable adjustment of the temperature of the spinning solution and/or of the evaporative power of the evaporative medium. In addition to adjusting the speed of the evaporative medium through the spinning cell customarily employed and to adjusting the temperature to which the evaporative medium is raised, the amount of solvent vapour contained in the evaporative medium controls to a comparatively small extent the evaporation of the solvent from the formed filaments or other products. For example it is customary to lead the evaporative medium charged with solvent vapours from the series of spinning cells or metier to a solvent recovery plant and then to return the evaporative medium still containing solvent vapour to the spinning cells. The content of solvent is therefore more or less dependent upon the efficiency of the solvent recovery apparatus and this content naturally controls to some extent the rate of evaporation of the solvent from the filaments in the cell. In the case of using a counter-current of evaporative medium, the latter is charged or further charged with solvent vapours before reaching the region of the spin-

ning nozzles. This again tends to retard evaporation. However, in all cases a very substantial evaporation of the solvent takes place before the filaments have travelled an appreciable distance from the spinning nozzle and in fact in general the filaments are solid almost at the point of extrusion or at least have a skin formed thereon.

In the present invention on the other hand in the immediate vicinity of the spinning nozzles and preferably for some considerable distance therefrom, for example for a matter of 2, 3, or 4 to 12 inches or more, the conditions are so adjusted that no evaporation of the solvent takes place, or at least the filaments or other products at the end of this first zone are still in a liquid or substantially liquid condition.

The evaporation of the solvent from the filaments or other products may be prevented in any suitable manner. The most effective means consists in spinning the filaments into a zone containing or not containing air or other gases or vapours and saturated or substantially saturated with the vapour of the solvent itself. Alternative or additional means for reducing or preventing evaporation comprise spinning a solution maintained at a temperature substantially below that customarily employed, for example at ordinary temperatures or temperatures below atmospheric. Again the air or other medium into which the spinning solution is spun may be cold or may be cooled to below atmospheric temperature, and in addition as a further means of reducing evaporation the speed of the air or other gaseous current, if any, may be reduced or such a current may be maintained at pressures above atmospheric.

As already indicated, the more or less liquid filaments or other products formed in the preliminary zone may be solidified by dry or wet methods or by a combination of the two. Where dry-spinning is employed throughout, the preliminary zone in which little or no evaporation of the solvent takes place and which is characteristic of the present invention is preferably separated almost completely from the remaining part of the spinning cell. Thus for instance an ordinary spinning cell or chamber may be provided with a diaphragm or partition defining the zone in which there is to be little or no evaporation. In the remainder of the cell any suitable conditions for evaporating the solvent and for producing the desired type of product, e. g. products of round cross-section and of dull or high lustre, may be maintained. The zone itself as already indicated may contain air or other gas under

pressure or not and may be saturated with acetone or other solvent employed in the spinning solution so as to reduce the evaporation, for example to nil or thereabouts. For this purpose acetone or other solvent may be injected into the zone containing more or less stagnant air or other gas, or alternatively the zone may contain liquid acetone or other solvent so as to maintain the atmosphere saturated with solvent or again a current of air or other gas saturated with acetone or other solvent may be passed through the said zone.

Instead of almost entirely separating the first or preliminary zone from the main part of the spinning cell, the spinning nozzle may be surrounded by a shield in the form, for example, of an inverted cup-shaped device, pipe, tube or other arrangement adapted to seclude the spinning nozzle from the main part of the spinning cell. By this means when spinning is first begun some evaporation of solvent takes place but the secluded atmosphere within the cup-shaped device or other arrangement rapidly becomes saturated with the solvent so that further substantial evaporation is avoided. If desired or requisite such device may be supplied with further quantities of solvent, as described above with reference to the separate zone, but such precautions are in general unnecessary.

The above forms of apparatus, and particularly that in which the spinning nozzle is surrounded or substantially surrounded by an inverted cup-shaped device, pipe, tube or other form of shield adapted to seclude the spinning nozzle from the main part of the spinning cell, form an important part of the present invention, which includes broadly such apparatus and the use thereof in dry or dry-and-wet spinning processes. The device for secluding the spinning nozzle may for example comprise a tube or the like and may be transparent or otherwise, and made of a heat conducting or non-conducting material, for example, of cardboard, mica, glass or transparent sheet material of cellulose acetate or the like or of tin, aluminium or other metal, or of copper or other metal gauze, preferably of fine mesh or made of a number of layers so as in effect to have a fine mesh. It may be formed in two halves so as to facilitate access to the nozzles or to facilitate assembly in the spinning cell or chamber and is preferably closed or substantially closed at the nozzle end. It may be heated or cooled as desired and may either merely serve to maintain the air or other medium immediately surrounding the nozzle stagnant or may be provided with injectors for the purpose of injecting solvents, swelling agents or non-solvents for the cellulose derivative, e. g. acetone, chloroform, the ethers of ethylene or other glycols, benzene, toluene, xylene, etc. The injection of such vapours or liquids may modify the strength, lustre, extension or other characteristics of the product, and is included within the scope of the invention. It is also within the scope of the invention to draw or otherwise pass a relatively slow current of air or other evaporative medium through the pipe, tube, cup-shaped device or other arrangement for secluding the nozzle.

Various forms of apparatus are illustrated in the accompanying drawings which are not to be regarded as in any way limitative.

Figure 1 is a longitudinal section of a spinning cell constructed in accordance with the present invention;

Figure 2 is an enlarged view of the filter candle

and shield assembly of the apparatus of Figure 1, showing the latter in the telescoped position;

Figure 3 is a view similar to Figure 2, but showing an alternative form of shield;

Figure 4 is a further view of the modifications shown in Figure 3, the shield being raised to facilitate access to the jet;

Figure 5 is a view similar to Figure 3, but showing means for passing a regulatable flow of air or vapor through the shield;

Figure 6 is an inverted cross-section of the apparatus of Figure 5, taken along the line 6-6 thereof;

Figure 7 is a longitudinal section of a further form of apparatus in which the shield is provided with heating means;

Figure 8 is a view similar to Figure 7, but showing a further modification of the shield;

Figure 9 is a cross-section of Figure 8 on the line 9-9 thereof;

Figure 10 is a view similar to Figure 8, but showing a further form of device for introducing air or vapor into the shield; and

Figure 11 is a longitudinal section of apparatus according to the invention including a bath for completing the setting of the filaments.

Fig. 1 represents a longitudinal section of a spinning cell 12 in which the jet 14 is surrounded by a shield 15 fitted to the filter candle 13. The apparatus is arranged to twist and wind the filaments and the like for example by the cap spinning or other suitable method. The shield which is telescopic in form is shown fully extended in Fig. 1. In Fig. 2 it is shown in the closed position, permitting of ready access to the jets. The sleeve will be described in detail with regard to Fig. 2. The cell in Fig. 1 is provided at 16 with an inlet for the evaporative medium, and at 17 with an adjustable outlet therefor. The cell may be heated by any suitable means, for example by means of the heating pipes 18. The filaments 19 emerging from the jet 14 pass round a guide 19' through an opening 20 in the side of the cell, round a feed roll 21 and guide 22 and are collected by means of the cap spinning device 23, or any other suitable collecting device.

Referring to Fig. 2, the sleeve or tube 24 is fitted to the candle 13 by means of a ring 25 which is rigidly attached to the sleeve and forms a sliding fit with the candle. A second sleeve 26 is fitted outside the first sleeve, being rigidly attached to a ring 27, which makes a sliding fit with the inner sleeve 24. In the same way a third sleeve 28 is attached by means of the ring 29 to the second sleeve 26. The actual number of sleeves of which the shield is built up may be varied according to circumstances.

Fig. 3 shows a simple form of shield comprising a cylindrical tube or sleeve 30 fitted round the filter candle 13 by means of a ring 31, which is rigidly attached to the filter candle and forms a sliding fit with the inside of the tube or sleeve. This arrangement allows the sleeve to be raised from the position shown in Fig. 3 to that shown in Fig. 4, which represents the same apparatus with the sleeve in a position which renders the jets accessible for cleaning. The lower end of the sleeve is provided with a disc 32 in which is an aperture 33 through which the filaments 19 emerge, said disc being retained in position by means of a ring shaped member 34 screwed on to the lower end of the sleeve. The tube 30' may if desired be employed to introduce or remove air, solvent or non-solvent vapours, or other gaseous media.

Fig. 5 represents a type of shield provided with means for regulating the supply of air or vapour or other gaseous media at a particular region within the shield. The sleeve 35 is secured to the outside of the filter candle 13 by means of two set screws 37. The ring 36 which is rigidly attached to the filter candle forms a sliding fit with the inside of the sleeve.

Fig. 6 shows an inverted plan cross-section of the apparatus along the line 6—6 of Fig. 5. The sleeve is perforated at 38. Two hollow members 39 and 40, the former attached to the inlet tube 41, the latter to the outlet tube 42, are fixed in position on the outside of the sleeve so as completely to cover the perforations 38. Each of the members 39 and 40 is provided with baffle plates 43. In order to facilitate the regulation of the pressure within the sleeve 35 the inlet pipe 41 is provided with a pressure gauge 44, while the outlet pipe 42 is provided with a suction gauge 45. The arrangement is such that a stream of air, vapour or other gaseous medium may be directed upon the filaments or the like, at a point depending upon the position in which the sleeve is fixed by means of the set screws 37.

Fig. 7 represents a shield provided with external heating means, the apparatus being such that very rapid preliminary drying of the filaments can be obtained. The sleeve 46 is attached to the outside of the filter candle 13 by means of two rings 47 and 48. The sleeve is open at the lower end, through which the filaments 19 from the jet 14 emerge. The sleeve is surrounded by a heating or cooling coil 49, and steam, air, oil, brine or other suitable heating or cooling medium enters the coil by means of the inlet tube 50, and issues therefrom by means of the outlet 51.

Fig. 8 represents a longitudinal section through a shield provided with means for regulation of the air, vapour or other gaseous medium admitted to the zone within the shield. Fig. 9 represents an inverted plan cross-section through the apparatus along the line 9—9 of Fig. 8. The sleeve 52 is attached by means of a ring 53 to a filter candle 13, the ring being rigidly attached to the filter candle and making a sliding fit with the inside of the sleeve. At intervals along the length of the sleeve are radial apertures 54. The drawing shows three rings of such apertures. Three spring clips 55 are fitted around the outside of the sleeve and are capable of completely covering the apertures therein. These clips are provided with radial apertures 56 and by rotating the clips into a suitable position the apertures therein may be made to register with the apertures in the sleeve. In this way the maximum interchange of atmosphere between the inside and outside of the shield is obtained. On the other hand the clips may be rotated so as completely or partially to close the apertures in the sleeve, so cutting off or limiting the interchange of air, vapour or other gaseous medium between the inside and the outside of the sleeve. In Figs. 8 and 9 the clips are shown in such a position that maximum interchange is possible. The ends of the clips are turned up at 57 so as to facilitate rotation of the sleeve into the desired position.

Fig. 10 represents a shield provided with alternative means for regulation of the atmosphere inside. A sleeve 58 is attached to the filter candle 13 by means of a ring 59 which is rigidly attached to the outside of the filter and forms a sliding fit with the inside of the sleeve. The lower end of the sleeve is open to permit the filaments to emerge. Located within the shield is a

vertical tube 60 which is provided with nozzles, jets or perforations 60' so located that a stream of air, vapour or other gaseous medium may be directed on to the filaments 19 or into the atmosphere in the neighbourhood thereof.

Fig. 11 represents in longitudinal section an apparatus in which partially coagulated filaments obtained in the cell are passed therefrom into a coagulating bath. The cell 61 is provided with a filter candle 13 and a jet 14. The filter candle is surrounded by a shield 58 of the same type as is shown in Fig. 10. By means of the perforated tube 60 the atmosphere within the shield 58 may be maintained sufficiently rich in the vapours of the solvent employed in the spinning solution for the filaments emerging from the shield to have undergone little or no coagulation. Heating means are provided at 18. The evaporative medium enters the cell through the inlet pipe 16 and issues therefrom through the outlet pipe 17 which is provided with regulating means. The conditions with regard to temperature and flow of evaporative medium are so adjusted with respect to the length of the metier that the filaments 19 emerging from the aperture 62 have undergone relatively little coagulation. From the aperture 62 the filaments pass into a bath 63 containing a suitable coagulating medium 64. The filaments pass around the thread guide 65 situated in the bath, and on emerging from the bath are carried by the feed roller 66 to a suitable collecting device, for example a spinning pot.

The invention includes processes and apparatus in which the spinning, or at least the initial part of the spinning is either upward or downward and in which air or other evaporative medium flows in counter-current to or in the same direction as the filaments or other products.

Among the wet coagulation methods which may be applied in treating the more or less liquid filaments, ribbons or other products issuing from the zone characteristic of the invention, special mention may be made of those described in U. S. Patents Nos. 1,465,994 and 1,467,493 and U. S. application S. No. 402,785 filed October 26, 1929, which describe spinning into coagulating baths containing solvents or latent solvents for the cellulose derivative in small or large concentrations. Such baths may further contain salts, sugars, or other suitable additions as described in U. S. application S. No. 469,622 filed July 21, 1930. Any other suitable coagulating bath may however be employed, for example sulphuric acid or other strong mineral acid or mineral acid ester, as described in U. S. application S. No. 431,966 filed February 27, 1930, or organo mineral acids, e. g. sulphonic acids as described in U. S. application S. No. 450,871 filed May 8, 1930.

The filaments or other products formed by dry or wet methods as described above may be passed round a feed roller or other device adapted to apply tension thereto, and in fact it is found that by reason of the preliminary zone, which is characteristic of the present invention, the filaments or other products can be drawn out to produce very fine deniers or low cross-sections indeed.

The filaments or other products produced according to any of the above methods may be further treated in any desired manner to impart improved properties thereto. For instance, they may be stretched when in the finished condition, whether or not they have been drawn out or stretched during formation, so as to obtain still further increased strength. Again they may be treated according to the process described in U. S.

application S. No. 552,420, filed July 22, 1931, corresponding to British application No. 22,895/30 filed July 30, 1930 with or without stretching. This specification describes impregnating the materials with relatively dilute solutions of solvents or softening agents, and subsequently concentrating the solutions on the material so as to enable them to exert a solvent action thereon. Examples of suitable solvents or softening agents are aqueous solutions of thiocyanates, such as those of the alkalis, ammonium and alkaline earths, aqueous solutions of zinc chloride, acetic acid, formic acid, lactic acid, diacetone alcohol, methyl or ethyl lactate, acetone, and the like; and mono- and di-ethers of olefine glycols and polyolefine glycols, for instance the mono- and dimethyl and ethyl ethers of ethylene glycol, dioxane, the mono-ethyl and ethyl ethers of propylene glycol, and the mono-ethyl ether of diethylene glycol, etc; phenols, formaldehyde, acetaldehyde, mono-, di- and tri-acetins, di-chlorethylene, and the like, mineral acids, sulphonic or other organo-mineral acids, or acid esters of mineral acids or mixtures of these, or solvent mixtures. The agent with which the filaments or threads are treated may be diluted with a liquid or diluent which is not a solvent of the cellulose derivative, for instance water, benzene, or the like. The solvent action may be exerted on the filaments or other products with or without simultaneous stretching.

The invention is broadly applicable to the production of filaments, threads, and other products, etc. from solutions of any suitable cellulose derivatives, for example cellulose acetate or other esters of cellulose, e. g. cellulose acetate, nitroacetate, formate, propionate, butyrate and the like or other esters of cellulose, e. g. cellulose nitrate, and cellulose ethers, for instance methyl, ethyl or benzyl cellulose, or ether-esters of cellulose.

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

1. Process for the production of artificial materials, comprising extruding spinning solutions containing cellulose derivatives into an atmosphere in which substantially no evaporation of the solvent occurs so that the extruded products in passing through said atmosphere remain liquid and then passing the extruded products into an evaporative atmosphere.

2. Process for the production of artificial materials, comprising extruding spinning solutions containing cellulose acetate into a substantially isolated space in which evaporation of the solvent is substantially prevented by the presence of the vapor of the solvent and passing the extruded products into an evaporative atmosphere.

3. Process for the production of artificial materials, comprising extruding spinning solutions containing cellulose acetate into an atmosphere secluded from the main body of the atmosphere in the spinning cell, said secluded atmosphere being maintained at such a temperature below the temperature of said main body of atmosphere that substantially no evaporation of the solvent occurs and finally setting the resulting artificial materials.

4. Process according to claim 2, in which solvent vapors are continuously introduced into the substantially isolated space.

5. Process according to claim 2 in which a slow current of evaporative medium is continuously introduced into the substantially isolated space.

6. Process for the production of artificial ma-

terials, which comprises passing a stream of an evaporative atmosphere through a spinning cell, trapping a central portion of said stream to form a pocket of substantially stagnant atmosphere, causing substantial saturation of said pocket with the vapors of a solvent, and extruding a solution of a cellulose derivative in said solvent through fine orifices discharging directly into said pocket, so that the filaments so formed pass from a substantially non-evaporative atmosphere into an evaporative atmosphere.

7. Process for the production of artificial materials, which comprises passing a stream of an evaporative atmosphere through a spinning cell, trapping a central portion of said stream to form a pocket of substantially stagnant atmosphere, causing substantial saturation of said pocket with the vapors of a solvent, and extruding a solution of a cellulose acetate in said solvent through fine orifices discharging directly into said pocket, so that the filaments so formed pass from a substantially non-evaporative atmosphere into an evaporative atmosphere.

8. Apparatus for the production of artificial filaments and like materials by the evaporative method from solutions of cellulose acetate or the like, comprising a spinning cell, a spinning jet in the cell and a shield device, surrounding said jet, constructed and arranged to maintain a stagnant atmosphere in the neighborhood of the jet, and to isolate it from the remainder of the cell.

9. Apparatus for the production of artificial materials comprising a spinning jet, a filter candle communicating with said jet, a shield attached to said candle, said shield being constructed and arranged to seclude and maintain in a stagnant condition the atmosphere in the neighborhood of the spinning jet and means for producing an evaporative atmosphere for setting the materials extruded from said jet.

10. Apparatus for the production of artificial filaments and like materials by the evaporative method from solutions of cellulose acetate or the like, comprising a spinning jet, a candle filter communicating with said jet, a shield adjustably attached to said candle filter, said shield being constructed and arranged to seclude and maintain in a stagnant condition the atmosphere in the neighborhood of the spinning jet, and means for producing an evaporative atmosphere for setting the materials extruded from said jet.

11. Apparatus for the production of artificial filaments and like materials by the evaporative method from solutions of cellulose acetate or the like, comprising a spinning jet, a candle filter communicating with said jet, a shield comprising a sleeve slidably mounted upon a ring rigidly attached to said candle filter, said shield being adapted to seclude and maintain in a stagnant condition the atmosphere in the neighborhood of the spinning jet, and means for producing an evaporative atmosphere for setting the materials extruded from said jet.

12. Apparatus for the production of artificial filaments and like materials by the evaporative method from solutions of cellulose acetate or the like, comprising a spinning jet, a candle filter communicating with said jet, a shield comprising a number of tubes sliding one within the other attached to said filter, said shield being adapted to seclude and maintain in a stagnant condition the atmosphere in the neighborhood of the spinning jet, and means for producing an evaporative

atmosphere for setting the materials extruded from the said jet.

13. Apparatus for the production of artificial filaments and like materials by the evaporative method from solutions of cellulose acetate or the like, comprising a spinning cell, a spinning jet in the cell, a shield device, surrounding said jet, constructed and arranged to maintain a stagnant atmosphere in the neighborhood of the jet, and to isolate it from the remainder of the cell, and means for introducing a vapor or gaseous medium into the chamber surrounding the jet.

14. Apparatus for the production of artificial filaments and like materials by the evaporative method from solutions of cellulose acetate or the like, comprising a spinning cell, a spinning jet in said cell, a shield device, surrounding said jet, constructed and arranged to maintain a stagnant

atmosphere in the neighborhood of the jet, and to isolate it from the remainder of the cell, and means for attemperating the atmosphere surrounding the jet.

15. Apparatus for the production of artificial materials comprising, in combination, a spinning cell, means for passing a stream of an evaporative atmosphere through said cell, a cup-shaped member situated wholly in said stream so as to trap and maintain a pocket of substantially stagnant atmosphere in the midst of the stream, a spinning jet discharging within the cup-shaped member, and means for extruding a spinning solution from said jet through said cup-shaped member into the evaporative stream.

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