

Dec. 7, 1943.

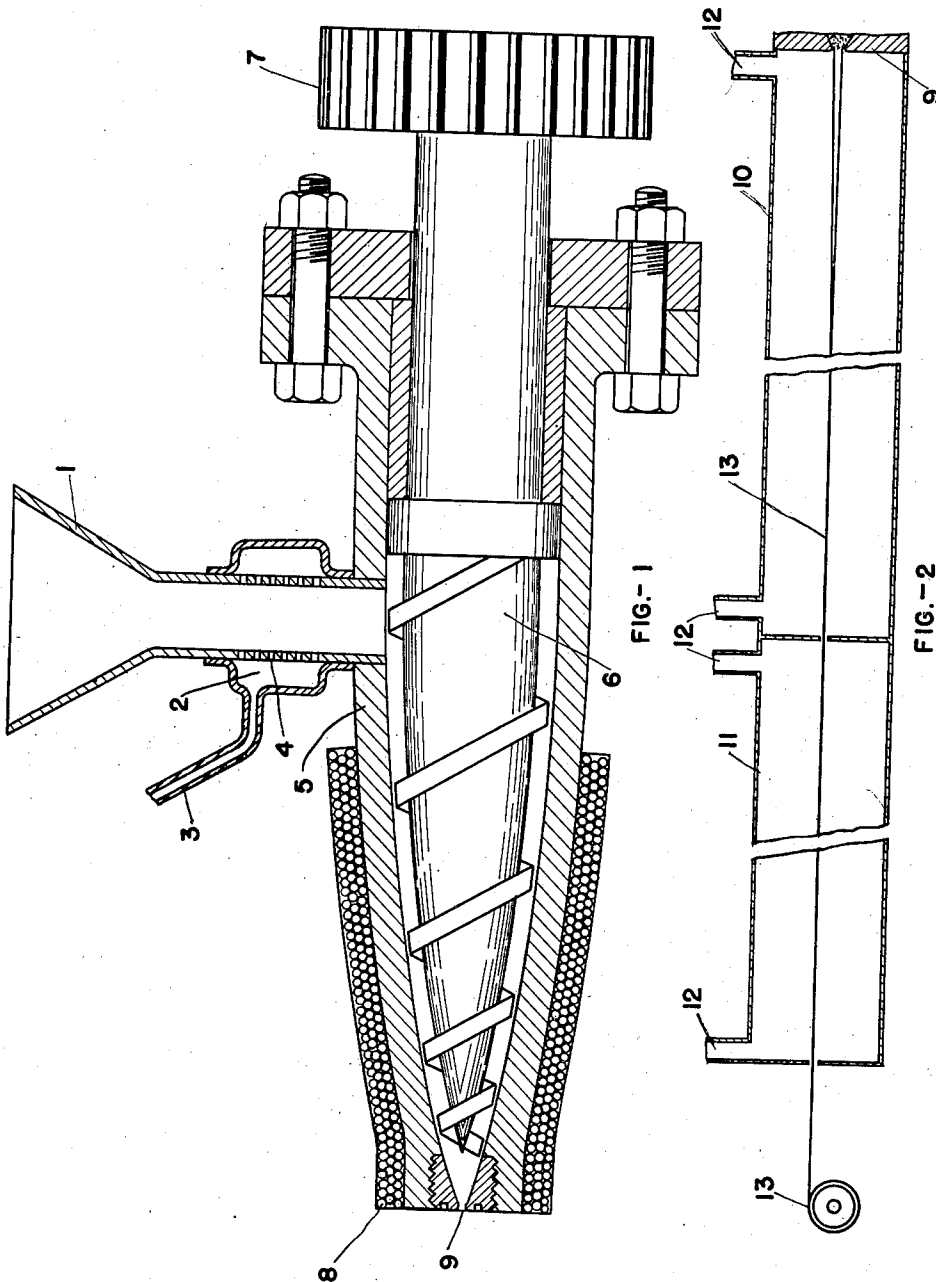
L. N. BENT

2,336,159

METHOD OF PREPARING FILAMENTS

Filed Sept. 25, 1940

2 Sheets-Sheet 1



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Dec. 7, 1943.

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METHOD OF PREPARING FILAMENTS

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2 Sheets-Sheet 2

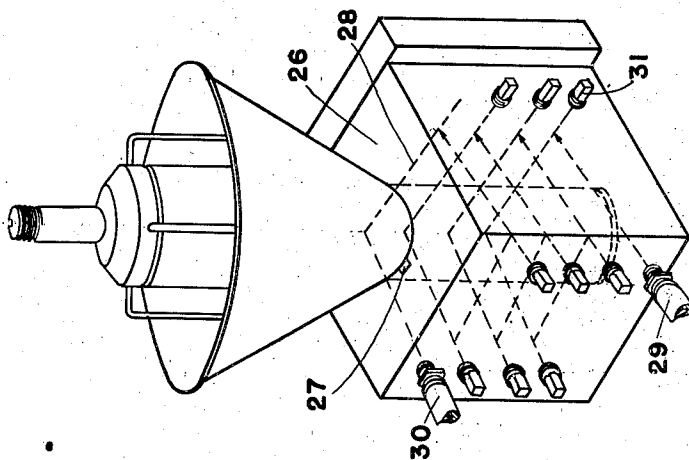


FIG-8

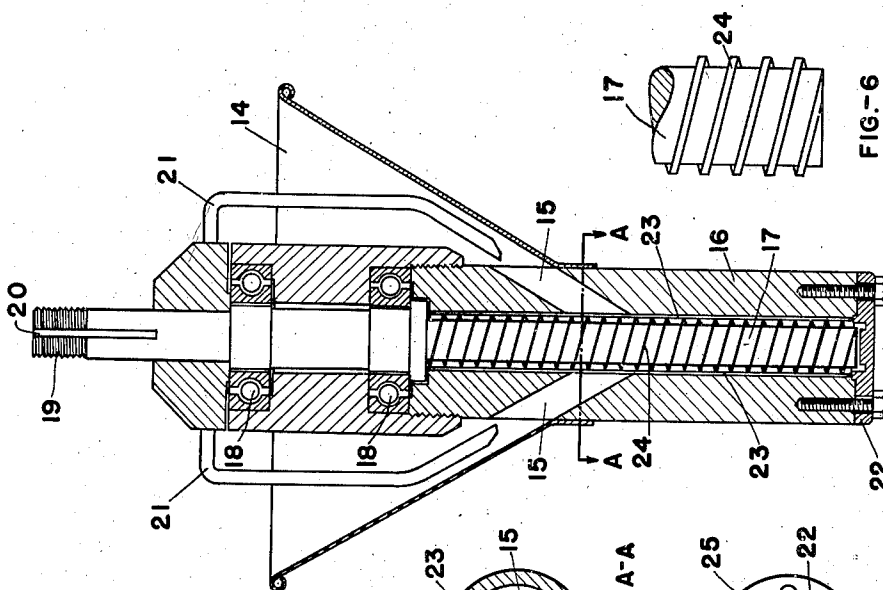


FIG-3

SECTION A-A
FIG-5

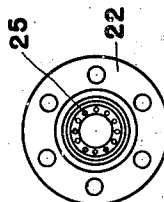
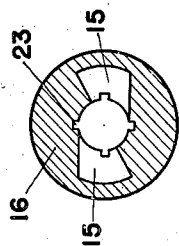


FIG-7

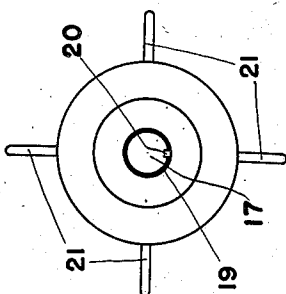


FIG-4

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UNITED STATES PATENT OFFICE

2,336,159

METHOD OF PREPARING FILAMENTS

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Application September 25, 1940, Serial No. 358,225

25 Claims. (Cl. 18—54)

This invention relates to a method for the preparation of thin filaments suitable for textile purposes and more particularly it relates to a method for the preparation of such filaments from lower fatty acid esters of cellulose entirely without the use of solvents or plasticizers.

Filaments have long been prepared from cellulose acetate by forming solutions thereof in volatile solvents, extruding the solutions, and eliminating the volatile solvent. It has been recognized that the use of solvents in this manner presents a number of disadvantages. A portion of the solvent is always lost and in addition, recovery of the major portion of the solvent is expensive. Furthermore, volatile solvents present fire, explosion, and toxicity hazards.

Cellulose acetate filaments prepared from solutions thereof have also had limitations in their properties. For example, higher strength and a higher softening temperature have been desired. These limitations in cellulose acetate textile filaments have, however, been inherent to some extent in the process by which they are prepared.

The use of solvents or plasticizers has always been considered necessary for the preparation of fine filaments from cellulose esters. So far as can be ascertained, the use of heat and pressure alone has never yielded useful textile filaments, probably because of the fact that it has long been the common belief of the art that cellulose esters decompose when heated in unmodified form to their softening points.

It is an object of this invention to provide filaments of cellulose acetate and other lower fatty acid esters of cellulose which are stronger than those heretofore obtainable. It is a further object to obtain filaments of the character mentioned by a method in which solvents and plasticizers are altogether eliminated. Other objects will appear hereinafter.

Now it has been discovered that, contrary to the established belief of the art, cellulose lower fatty acid esters can be spun into fine filaments suitable for textile purposes by extrusion thereof under the influence of heat and pressure only, followed by stretching of the extruded material, entirely without the use of solvents or plasticizers. Thus, in accordance with this invention, the above mentioned objects are attained by heating a lower fatty acid ester of cellulose to a plastic state extruding the heated ester through an orifice, stretching and cooling the extruded ester, limiting the time in which the ester is at elevated temperatures to a period insufficient to cause substantial decomposition of the ester.

The heat required is applied to the cellulose ester at a rate sufficient to bring it to a temperature at which it is in a plastic or semi-fluid state in a period of time which is shorter than that required to bring about substantial decomposition of the ester. In addition, the extrusion and cooling operations are accomplished with sufficient promptness so that the cellulose ester remains throughout the total process at elevated temperatures which would normally cause decomposition for a total period insufficient to cause substantial decomposition. The stretching operation is applied before or during the cooling operation, or if desired, after at least partial cooling. Preferably, it is applied during the cooling of the extruded cellulose ester.

By means of this invention substantially unmodified, i. e. unsoftened, cellulose lower fatty acid esters such as cellulose acetate may be spun to form fine textile filaments without the use of solvents or plasticizers, thereby obviating the expense and other disadvantages inherent in their use. The danger of non-uniformity and other disadvantageous effects caused by residual solvent in the filaments in variable amount is eliminated. The filaments obtained are stronger than those obtained by other processes. Furthermore, these advantages are obtained without substantial heat decomposition of the cellulose esters utilized, even though the esters are exposed for a brief time to temperatures which would normally cause decomposition.

The cellulose lower fatty acid ester suitable for the method of this invention may be such as, for example, cellulose acetate, cellulose propionate, cellulose acetate propionate, cellulose acetate formate, cellulose acetate butyrate, and the like. The cellulose ester utilized will be of the type which is soluble in the usual organic solvents. The degree of substitution will vary somewhat according to the particular ester utilized. For example, in the case of cellulose acetate, the combined acetic acid content may be within the range from about 48.5% to that corresponding to the normally obtainable tri-ester, the preferred value being in the range from about 52 to about 57% acetic acid. For other cellulose lower fatty acid esters, a somewhat equivalent degree of substitution is suitable. The viscosity of the cellulose lower fatty acid esters may be varied within wide limits but, in general, the viscosity of the order of that at present used for the preparation of artificial silk and the like is suitable. In general, the higher the viscosity of the ester, the stronger will be the product. The physical form

of the cellulose ester is preferably that of fine, dense grains; desirably clean, uniform cellulose esters of high stability, free of residual solvent and other modifiers or impurities are utilized.

The period of time during which the cellulose lower fatty acid ester may be held at an elevated temperature depends upon the temperature. As is well known, cellulose esters decompose upon being heated, following the course of depolymerization, discoloration, loss of acid groups, and caramelization. However, it has now been found that the cellulose lower fatty acid esters, unlike most chemical compounds, do not have a true decomposition temperature. Instead, they have a certain rate of decomposition at each temperature. It has been found that the cellulose lower fatty acid ester can thus be spun into filaments at unexpectedly high temperatures such as 425 to 550° F. at which decomposition is normally caused to take place, with only slight depolymerization if the steps of heating, shaping, and cooling are expeditiously carried out. Slight depolymerization is harmless, although extensive depolymerization is detrimental to the strength of the product.

Depolymerization is easily measured by determining the viscosity of the cellulose ester in solution, for example, by determining the specific viscosity of an 0.5% solution in dioxan with an Ostwald capillary viscometer as hereinafter described. In general, a 10% loss of specific viscosity is considered slight and harmless; a 25% loss would not be excessive for some uses; but more than a 50% loss would greatly reduce the usefulness of the cellulose ester. Taking the properties of cellulose acetate as exemplary of the lower fatty acid esters, it has been found that cellulose acetate having a reasonably high stability may be heated about 40 minutes at 390° F., or for about 15 minutes at 445° F., or for about 4 minutes at 500° F., or for about 2 minutes at 560° F. in an inert atmosphere without causing more than about a 10% loss in specific viscosity.

It will be appreciated that since the rate of depolymerization of cellulose lower fatty acid esters varies with temperature, and since the temperature of the ester varies during its treatment in accordance with this invention, no exact time limits can be set for the period during which the cellulose ester may safely remain in the heating state. Desirably, the treatment of the cellulose lower fatty acid ester in accordance with this invention is so conducted that the combined effect of time and temperature for all steps will be effective to decrease the specific viscosity of the ester by no more than about 10%. In no case should the combined effect of time and temperature be a decrease of the specific viscosity by more than 50%.

The rate of decomposition as measured by the loss in specific viscosity is, it has been found, affected by the environment or atmosphere in which the cellulose ester is heated. It is about twice as rapid in air as in an inert atmosphere such as, for example, an atmosphere of argon, nitrogen, carbon dioxide, mixtures thereof, and other gases or vapors non-reactive with cellulose ester. A vacuum is also considered herein to constitute an inert atmosphere or environment. Preferably, but not essentially, in carrying out my invention, the cellulose ester is maintained in an inert atmosphere or environment such as described while it is at elevated temperatures. It is desirable to remove substantially

all air from the cellulose ester before heating by evacuation, or by flushing with an inert gas, or both.

The temperature to which the cellulose lower fatty ester is heated in the method according to this invention will be sufficient to render plastic or semi-fluid the cellulose ester so that it will flow under pressure and be capable of extrusion to form tough, flexible filaments. However, the temperature will be less than that causing substantial decomposition within a period of time; for example, one minute, sufficient for carrying out the method of the invention. The actual temperature to be utilized varies with the particular ester which is being spun, and also with the degree of substitution of the ester. It may further vary somewhat with the equipment being utilized. In general, temperatures in the range from about 425° F. to upwards of about 560° F. have been found suitable with the equipment of the type hereinafter described.

The temperature to which the cellulose lower fatty acid ester is heated and at which it is extruded may be exemplified more particularly by reference to conditions utilized in spinning cellulose acetate. Utilizing the particular equipment hereinafter described for spinning cellulose acetate having a combined acetic acid content of 53 to 54%, a temperature in the range, for example between 500° F. and about 540° F. was found to be most suitable, although temperatures somewhat higher and somewhat lower gave a useful product. It has been found that for cellulose acetate having a higher or a lower degree of substitution than the 53 to 54% acetic acid content mentioned, it is desirable to utilize higher temperatures varying roughly in proportion to the increase or decrease in substitution from that mentioned. The temperatures suitable for other cellulose lower fatty acid esters are similar, except that as the quantity of acyl groups having a higher number of carbon atoms than the acetyl group is increased, the temperature of operation may be decreased. It is in general preferable to provide a maximum of mechanical force or pressure for the extrusion step, heating to a temperature fairly low in the operative range for the particular ester utilized. However, it must be kept in mind that material extruded at too low a temperature produces useless, worthless, brittle filaments unsuitable for textile purposes, so that temperatures must in all cases be sufficiently high to allow extrusion to useful, flexible filaments.

Cooling may be accomplished by merely permitting the extruded filament to disperse its heat to its surroundings, or cooling may be hastened by providing a stream of cool air or other cooling fluid to extract the heat more rapidly from the extruded filament. It will be understood that where cooling is specified, it will include either accelerated cooling or cooling by normal dispersion of heat to the atmosphere into which the cellulose ester is extruded.

After the cellulose lower fatty acid ester has been heated and extruded, the extruded material is stretched in order to obtain fine filaments having the desirable properties obtained through the use of the method in accordance with this invention. Stretching is accomplished by reeling the extruded ester at a velocity which is greater than that of the material while it is in the orifice through which it is extruded. Stretching is preferably carried out while the extruded material is cooling or is being cooled, although it may be

carried out advantageously before cooling or to a limited extent after cooling. The temperature at which the stretching is carried out may be that utilized in the extruding step, or as in most cases, a somewhat lower average temperature will prevail. Thus, stretching temperatures between about 200° F. and about 560° F. may be utilized. The degree of stretching will depend upon the diameter of the orifice through which the cellulose ester is extruded and upon the ultimate properties desired in the fine filament prepared. In general, the degree of stretching which is defined as the ratio of the cross section of the material in the orifice to the cross section of the final stretched filament, will be at least about three and may be 1000 or more at very high temperatures. Particularly good results in the formation of fine strong filaments are obtained utilizing a degree of stretching from about 50 to about 300.

The orifice through which the cellulose lower fatty acid ester is extruded may vary in diameter according to the nature of the ester being spun and the conditions of operation. Orifice diameters between about 0.001 inch and about 0.020 inch have been found suitable, diameters between about 0.005 inch and about 0.0012 inch leading to expedient operation. For relatively large orifices such as 0.010 inch, the orifice wall may be straight or partially countersunk; for small orifices hyperbolic entrances are desirable.

Having now indicated the nature and purpose of this invention, there follows a description of exemplary apparatus suitable therefor with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic sectional view showing one form of an apparatus suitable for heating and extruding a single filament of a cellulose ester being spun in accordance with the method of this invention.

Figure 2 is a diagrammatic sectional view of an apparatus suitable for the cooling and stretching steps.

Figure 3 is a simplified sectional view showing a second form of apparatus suitable for carrying out the heating and extruding steps of this invention in a manner whereby a multifilament yarn may be produced.

Figure 4 is a top view of the apparatus shown in Figure 3.

Figure 5 is a cross-sectional view of the apparatus shown in Figure 3.

Figure 6 is an enlarged fragmentary view of the extrusion screw utilized in the apparatus shown by Figure 3.

Figure 7 illustrates a spinneret which may be used with the apparatus shown in Figure 3.

Figure 8 is a pictorial schematic view of extruding apparatus such as that shown in Figure 3 in assembly with a heat-supplying device.

Referring to Figure 1, element 1 is a hopper provided with an annular chamber 2 which may be fed by a gas through tube 3 and which communicates with the hopper through perforations 4. The hopper leads into the extrusion barrel 5. The element 6 is a screw fitted into the barrel and actuated through the gear 7, which is in turn driven by gearing not shown in the drawings. The coil 8 carries electrical current for heating the apparatus, and it may be of the induction or resistance-heating type. The barrel is provided with an orifice fitting 9 having in this case a single orifice. It will be appre-

ciated that Figure 1, as well as other figures of the drawings, are diagrammatic, and that for the sake of clarity many details such as driving equipment, supporting frames, electrical controls and temperature-indicating equipment such as thermocouples have been omitted.

The apparatus of Figure 2 is auxiliary equipment which may be utilized with extruding equipment, for example that shown in Figure 1. The element 9 represents an extrusion orifice fitting which may be of the single orifice or of the multi-orifice type. The apparatus of Figure 2 comprises elongated chambers 10 and 11 provided with inlet and outlet fittings 12 adapted to provide a current of temperature-regulating gas or other fluid, and provided with suitable openings for a filament or yarn 13. The reel 13 is adapted to be driven at controlled peripheral speeds to take up and stretch extruded filaments.

In preparing fine filaments in accordance with this invention utilizing for example the apparatus of Figures 1 and 2, the cellulose ester is fed down the relatively narrow and deep hopper into the extrusion barrel. Preferably, it is met during its flow down the hopper by a countercurrent stream of an inert gas, such as carbon dioxide or nitrogen which may be heated if desired, say to 250-360° F. to pre-heat the ester. If desired, the entire hopper system may be placed under a vacuum. The ester is forced along the barrel of the extruder by the screw. It is progressively heated to a plastic or semi-fluid state by contact with the heated walls of the barrel. The temperature of the barrel and the quantity of heat provided by the heating means are regulated with respect to the rate of feed of the cellulose ester, so that the material reaches the desired plastic state at the time it reaches the orifice or slightly prior thereto. The material progresses to the orifice and is extruded there-through. It is then taken up by a reel or bobbin having a controlled peripheral velocity which is greater than the velocity of the cellulose ester in the orifice. The extruded filament may be in open air between the orifice and the take-up reel, but preferably it passes through heat controlled chambers such as are shown in Figure 2. The heat controlled chambers may be provided with a current of carbon dioxide, nitrogen, or other fluid at a controlled temperature. If desired, the filaments may be maintained at an elevated temperature in the first chamber and cooled by cooling fluid in the second chamber. The degree of stretch imparted to the filament is controlled by regulating the speed of the extrusion screw and the peripheral velocity of the take-up reel so that the extruded material has the desired higher velocity at the take-up reel as compared with its velocity in the orifice.

Figure 3 illustrates equipment designed for the spinning of a multiple-filament yarn in accordance with the method of this invention. In Figure 3 the element 14 is a hopper leading through ports 15 into the internal portion of the extrusion barrel 16. The barrel is fitted with a screw 17 shown schematically. The screw is provided with suitable bearings 18 adapted to absorb thrust forces while maintaining the screw in proper position in the barrel and allowing it to rotate therein. The screw is further provided with means consisting of thread 19 and keyway 20 for attaching driving devices such as gears. Rigidly attached to the screw are kickers 21 adapted by rotation with the screw to insure con-

tinuous feed of the cellulose ester through the lower portions of the hopper. The lower end of the extrusion barrel is provided with a spinneret or orifice plate 22 provided with a plurality of orifices (not shown in Figure 3) through which the cellulose ester is extruded. A top view of the apparatus shown in Figure 3 is given by Figure 4 which omits the hopper but shows the arrangement of the kickers 21. The construction of the barrel at the entrance of the feeding ports into the interior thereof is shown by the cross-sectional view, Figure 5, which is taken along line AA of Figure 3, the hopper section being omitted. Referring to Figure 5 (and also to Figure 3), the four grooves 23 in the barrel provide a means for the escape of air or entrapped gases from the cellulose ester being compacted and fused into a plastic state.

An enlarged fragment of the screw 17 is shown by Figure 6, which shows in more detail the nature of the square threads 24 utilized. It will be noted that screw 17 is of the double-pitch type, although it may be of single or multi-pitch construction. The height of the threads of screw 17 is progressively decreased while maintaining the outside diameter and clearance thereof with respect to the interior of the barrel constant, as one progresses down the screw from the point of entrance of the cellulose ester into the extrusion barrel to the end of the screw nearest the orifice fitting. In this manner allowance is made for the increasing compactness of the cellulose ester as it is heated and rendered plastic during its traverse along the barrel.

The spinneret or orifice fitting is further illustrated by the view thereof in Figure 7, which shows the plurality of orifices 25.

Figure 8 provides a pictorial, schematic view of the extrusion equipment provided with a heat-supplying device. The extruder is held in the metal block 26 by means of a key 27. The block is provided with passages for the circulation of a heating fluid following the schematically indicated path 28 through the block from the inlet pipe 29 to the outlet pipe 30. The fluid-conducting passages are made by boring from the sides of the block and closing the openings as shown by plugs 31 where necessary. It will be appreciated that only a limited number of the plugs has been shown for the sake of clarity.

The apparatus shown in Figures 3-8 may be utilized in spinning fine filaments in accordance with this invention in the same manner as hereinabove described for the apparatus of Figure 1. The extruded filaments may be led through the open air to a take-up reel or preferably equipment such as that illustrated by Figure 2, used in conjunction with that shown by Figure 3. It will be understood that the heating means shown in Figure 8 may be replaced by heating jackets, or by electrical heating coils of the character shown in Figure 1, or by other means.

The examples following are given in illustration of specific operational procedures for the preparation of fine filaments in accordance with this invention.

Example I

Ground flake cellulose acetate having a particle size which permitted it to pass through a 35 mesh screen and having a combined acetic acid content of 53.1% was fed into the apparatus illustrated by Figures 3 to 8 inclusive. The cellulose acetate was fed through the hopper into the barrel along which it was forced by the ex-

trusion screw. The cellulose acetate was heated during its passage through the barrel to a temperature of approximately 510° F. in an elapsed time of three minutes and was extruded at about the said temperature in less than one additional minute. The cellulose acetate attained a plastic state suitable for extrusion during its passage along the barrel, being compressed during this time to eliminate entrained gas (principally air), and finally was extruded through the spinneret at the end of the barrel. The spinneret utilized was provided with 25 straight-walled holes, each 0.010 inch in diameter. From the outer face of the spinneret there issued 25 cellulose acetate filaments. The filaments were led to a bobbin which was revolved with a surface velocity of 15.24 meters per minute, which velocity was thereby imparted to the filaments at the bobbin. In this manner, the filaments were drawn or stretched while still hot and plastic, and during the cooling thereof to fine filaments of 5.4 denier each (0.00087 inch diameter). Thus the degree of stretching was 132. In this manner a thread of cellulose acetate containing 25 filaments, each filament 5.4 denier, was obtained. The filaments were found to be uniform, round in cross section, and free from gas pockets. The tensile strength of the yarn so obtained was found to be 2.1 grams per denier. In this example, the cellulose acetate was spun in open air, and the cooling operation consisted of merely allowing the extruded filaments to cool in the open air as they passed from the spinneret to the bobbin.

Example II

In this example cellulose acetate such as that utilized in Example I was spun with equipment such as that used in Example I, except that the extruder and bobbin assembly was enclosed in a cabinet in which an atmosphere of carbon dioxide was maintained. The operation was carried out in a manner similar to that of Example I, except that the cellulose acetate traversed the length of the barrel in two minutes and was heated to approximately 536° F. The bobbin utilized for taking up and stretching the cellulose acetate filaments revolved with a surface velocity of 41 meters per minute. A yarn having 25 filaments, 6.8 denier (0.00104 inch diameter) each, was obtained. The tensile strength of the yarn was found to be 2.03 grams per denier.

Example III

Cellulose acetate propionate containing 33.3% of combined propionic acid and 15.3% of combined acetic acid and of a particle to pass through a 35 mesh screen, was spun into filaments in the manner of Example I. The cellulose acetate propionate was heated to 525° F., extruded and drawn out in air to filaments of 14.5 denier (0.00154 inch diameter) each. The yarn so obtained had a tensile strength of 2.76 grams per denier.

Example IV

In this example cellulose acetate was spun to a colored yarn obtained directly without necessity of the usual dyeing operation. One hundred parts of cellulose acetate like that utilized in Example I were mixed with one part of duPont Oil Orange 95902 by tumbling overnight. The mixture was then spun in the manner described in Example I. Approximately two minutes were required for the mixture to traverse the length of the screw and attain a temperature of 518°

F. The surface velocity of the bobbin utilized to stretch the dyed filaments was 16.75 meters per minute. Uniformly dyed filaments of 17 denier were obtained.

Example V

In this example an insoluble pigment was incorporated in the filaments in order to produce a material of reduced glassiness of luster and having a unique metallic sheen. Four hundred parts of cellulose acetate like that utilized in Example I were tumbled with one part of aluminum dust (pigment grade) in a rotating drum. The mixture was spun into filaments in the manner utilized in Example I, the material being heated to 550° F. and traversing through the barrel of the extruder in two minutes. The filaments were drawn from the spinneret at a bobbin speed of 28 meters per minute. In this manner, thread having 7.7 denier (0.0011 inch diameter) filaments with a unique, uniform gray metallic luster was obtained.

The method in accordance with this invention has the advantage of providing stronger filaments than those normally obtained by solvent spinning of the same materials. It provides a considerable economic saving through avoidance of volatile solvents. No residual solvent can be present in the filaments to decrease their softening point and otherwise to adversely affect their properties. In addition, soluble and insoluble dyes and pigments may be incorporated directly in the filaments to produce desirable color effects or to improve opacity or to adjust the luster of the filaments to any condition between a dull and a glassy appearance.

The term "specific viscosity" as used herein is defined as follows. The time required at 25° C. for an 0.5% solution of cellulose ester in dioxan to flow from mark to mark in an Ostwald capillary viscometer is determined. A similar time of flow is determined for dioxan alone in the same viscometer. The viscometer chosen for the tests should have a capillary of such size that the time of flow for dioxan is between about 75 and about 125 seconds. Specific viscosity is then defined by the expression:

$$\frac{\text{Time of flow of the 0.5\% solution}}{\text{Time of flow of dioxan}} \text{ minus one}$$

This application is a continuation-in-part of my copending application Serial No. 243,106, filed November 30, 1938.

It will be understood that the details and examples hereinbefore set forth are illustrative only, and that the invention as broadly described and claimed is in no way limited thereby.

What I claim and desire to protect by Letters Patent is:

1. A method for preparing thin filaments of a cellulose lower fatty acid ester without the use of solvents or plasticizers which comprises the steps of heating a cellulose lower fatty acid ester to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

2. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating

cellulose acetate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

3. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having above 48.5% combined acetic acid, to a temperature at which it is in a semi-fluid state, said temperature being between about 425° F. and about 560° F., extruding the cellulose acetate through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

4. A method for preparing thin filaments of cellulose acetate propionate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate propionate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

5. A method for preparing thin filaments of cellulose acetate butyrate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate butyrate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

6. A method for preparing thin filaments of a cellulose lower fatty acid ester without the use of solvents or plasticizers which comprises heating a cellulose lower fatty acid ester to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

7. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

8. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having above 48.5% combined acetic acid to a temperature at which it is in a semi-fluid state, said temperature being between

about 425° F. and about 560° F., extruding the cellulose acetate through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

9. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having from about 52% to about 57% combined acetic acid to a temperature at which it is in a semi-fluid state, said temperature being between about 500° F. and about 540° F., extruding the cellulose acetate through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

10. A method for preparing thin filaments of cellulose acetate propionate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate propionate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate propionate through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

11. A method for preparing thin filaments of cellulose acetate butyrate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate butyrate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate butyrate through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

12. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%, and protecting the cellulose acetate from access of air during at least a part of the time during which it is at an elevated temperature.

13. A method for preparing thin filaments of a cellulose lower fatty acid ester without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate propionate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%, and protecting the cellulose acetate propionate from access of air during at least a part of the time during which it is at an elevated temperature.

14. A method for preparing thin filaments of a cellulose acetate butyrate without the use of

solvents or plasticizers which comprises the steps of heating cellulose acetate butyrate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%, and protecting the cellulose acetate butyrate from access of air during at least a part of the time during which it is at an elevated temperature.

15. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having an acetic acid content above about 48.5%, to a temperature at which it is in a semi-fluid state, said temperature being between about 425° F. and about 560° F., extruding the cellulose acetate through an orifice and stretching the extruded material to a degree of at least three, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%, and protecting the cellulose acetate from access of air during at least a part of the time during which it is at an elevated temperature.

16. A method for preparing thin filaments of cellulose lower fatty acid esters without the use of solvents or plasticizers which comprises heating a cellulose lower fatty acid ester to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice and stretching the extruded material to a degree between about 50 and about 300, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

17. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having above about 48.5% combined acetic acid to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice and stretching the extruded material to a degree between about 50 and about 300, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

18. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having from about 52% to about 57% combined acetic acid to a temperature between about 500° F. and 540° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice and stretching the extruded material to a degree between about 50 and about 300, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

19. A method for preparing thin filaments of cellulose lower fatty acid ester without the use of solvents or plasticizers which comprises heating a cellulose lower fatty acid ester to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice having a diam-

eter between about 0.001 and about 0.020 inch and stretching the extruded material to a degree of at least 3, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

20. A method for preparing thin filaments of a cellulose lower fatty acid ester without the use of solvents or plasticizers which comprises heating a cellulose lower fatty acid ester to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice having a diameter between about 0.001 and about 0.020 inch and stretching the extruded material to a degree between about 50 and about 300, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

21. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having above about 48.5% combined acetic acid to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice having a diameter between about 0.001 and about 0.020 inch and stretching the extruded material to a degree of at least 3, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

22. A method for preparing thin filaments of cellulose acetate without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate having from about 52% to about 57% combined acetic acid to a temperature between about 500° F. and about 540° F. at which it is in a semi-fluid state, extruding the cellulose acetate through an orifice having a diameter between about 0.001 and about 0.020 inch and stretching the extruded material to a degree between about 50 and about 300, conducting the

said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

23. A method for preparing thin filaments of a cellulose lower fatty acid ester of modified luster without the use of solvents or plasticizers which comprises heating a mixture of particles of a cellulose lower fatty acid ester and a small amount of finely divided solid inert pigmentary material to a temperature between about 425° F. and about 560° F. at which the mixture assumes a semi-fluid state, extruding the material through an orifice and stretching the extruded material to a degree of at least 3, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

24. A method for preparing thin filaments of cellulose acetate of modified luster without the use of solvents or plasticizers which comprises the steps of heating a mixture of cellulose acetate particles with a small amount of finely divided solid inert pigmentary material to a temperature between about 425° F. and about 560° F. whereby the mixture assumes a semi-fluid state, extruding the material through an orifice and stretching the extruded material to a degree of at least 3, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

25. A method for preparing thin filaments of a cellulose lower fatty acid ester without the use of solvents or plasticizers which comprises the steps of heating cellulose acetate to a temperature between about 425° F. and about 560° F. at which it is in a semi-fluid state, extruding the cellulose ester through an orifice, stretching and cooling the extruded material in an atmosphere of inert gas, conducting the said operations within a period in which the combined effect of time and temperatures will be a decrease in specific viscosity of the ester of less than 50%.

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